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Effects of Scented Personal Care Products on Ozone Reactivity with Human Building Occupants

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Effects of Scented Personal Care Products on Ozone Reactivity with Human Building Occupants

by

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Thesis

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Master of Science in Engineering

The University of Texas at Austin

May 2018

Acknowledgements

I would first like to thank Dr. Richard Corsi for helping teach me the concepts behind my research – his guidance and knowledge was instrumental to my success as a student and researcher. I would also like to thank Dr. Atila Novoselac for helping me set up the testing environment for this research effort and for consulting with me on my future career and research goals. Dr. Neil Crain's expertise with lab measurement and analysis was a most welcome help as well as his honest insight at various steps along the path to completion of my research and this report. Lastly, I would like to thank my friends and colleagues of the indoor air quality team: Leigh Lesnick, Jonathan Gingrich, Michael Wade, and Sangeetha Kumar.

Abstract

Effects of Scented of Personal Care Products on Ozone Reactivity with Human Building Occupants

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The concentration of ground-level ozone in many cities is projected to increase in the coming years. The greater the concentration of ground-level ozone, the more ozone will enter building spaces through infiltration and ventilation. Once indoors, ozone reacts with other gas-phase pollutants, building materials, and human skin lipids. Studies in portable classrooms suggest that reactions between ozone and human skin lipids contribute more to the overall reduction in bulk indoor ozone concentration than previous research indicates. We hypothesize that the increased ozone uptake to occupants is due to the prevalence of body sprays like colognes and perfumes noted during field measurements in high school classrooms. Cleaning products, air fresheners, body sprays, and deodorants contain high concentrations of unsaturated volatile organic compounds called terpenes because terpenes, which are known for their pleasant-smelling fragrances. Ozone is a respiratory irritant and known asthmagen, but by-products from ozone/terpene reactions can be potentially more harmful. Terpenes, along with molecules present on indoor furnishings and human skin lipids, represent major sinks for indoor ozone. In this study, the terpene

compositions of multiple, common male body sprays are characterized. From this analysis, one particular body spray was chosen based on the concentration of terpene and terpene-related species it contained. The body spray's effects on the ozone deposition velocity to cotton clothing and human subjects was tested in a stainless steel environmental chamber by comparing the steady-state ozone concentrations with and without the body spray applied. The average ozone deposition velocity to humans without the body spray applied was found to be 16.2 m/s. When the body spray was applied, the value actually decreased to 14.7 m/s. This research shows that scented body sprays might not noticeably alter clothing's or a person's reactivity with ozone. However, results from portable classrooms and a test chamber indicate that humans might be more reactive in the presence of ozone than previous studies have found, particularly at higher AERs that reduce transport resistance for ozone interactions with humans in indoor spaces.

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Overview

THE ISSUE

The current daily maximum National Ambient Air Quality Standard (NAAQS) for ground-level ozone concentration is 70 ppb (EPA, 2015). Major cities in developed nations typically experience ozone concentrations of this magnitude or higher, especially in areas with high levels of traffic and intense solar radiation. Ground-level ozone concentrations are concerning not only because links have been established between bad ozone days and increased hospitalization/death rates (Burnett et al., 1997; Burnett et al., 2001; Bell et al., 2005; Zanobetti and Schwartz, 2008; Jerrett et al., 2009; Di et al., 2017), but because the main source of indoor ozone comes from infiltration and ventilation of outdoor air. Chronic exposures to concentrations consistent with those found indoors have been associated with the onset of asthma (McConnell et al., 2002), cardiovascular disease (Bell et al., 2004; Goudarzi et al., 2013), and chronic obstructive pulmonary disease (Khaniabadi et al., 2017).

While ozone is harmful, reactions between ozone and volatile organic compounds (VOCs) that tend to have higher concentrations indoors generate by-products that are potentially more harmful than ozone alone. Of considerable importance are reactions between ozone and a subclass of VOCs known as terpenes. Terpenes are added to cleaning agents as natural additives (Nazaroff and Weschler, 2004; Nørgaard et al., 2014) and in personal care products because of their pleasant-smelling fragrances (Corsi et al., 2007). By-products from ozone/terpene chemistry have been found to act as dermal allergens (Clausen et al., 2001), eye irritants (Nøjgaard et al., 2005), and carcinogens like formaldehyde (Salthammer et al., 2010). Since Americans on average spend nearly 90%

of their day indoors, more research is needed to ascertain the effects of indoor ozone chemistry between humans, their environment, and their personal care products.

OBJECTIVES

The overall objective of this research was to determine if the application of a common consumer body spray to a human subject would increase the ozone chemistry on and around the wearer. Specific objectives include:

1. Calculate the ozone decay rate and deposition velocity to a single student using ozone and carbon dioxide data gathered in multiple portable classrooms.
2. Calculate the ozone decay rate and deposition velocity to a single cotton T-shirt in a controlled environmental chamber.
3. Calculate the ozone decay rate and deposition velocity to the same T-shirt now with a common body spray applied in the same environmental chamber.
4. Perform the same experiments but with two different human subjects to determine the ozone decay rate and deposition velocity to a single human subject without and with the body spray applied.
5. Compare the values of ozone decay and deposition velocity without the body spray applied to those calculated in portable classrooms and found in other published studies.
6. Compare the values of the ozone decay rates and deposition velocities to T-shirts and humans without and with the body spray applied to see if there is an increase in ozone reactivity on and/or near the T-shirt or human.

GENERAL METHODOLOGY

Ozone Deposition Velocity in Portable Classrooms

The Healthy High School PRIDE (**P**artnership in **R**esearch on **I**n**D**oor **E**nvironments) study was the starting point for this research project. Carbon dioxide (CO_2) and ozone (O_3) were measured inside and just outside portable classrooms in the central Texas area. There were many objectives for the PRIDE study, one of which was to determine to what extent occupants influenced the ozone chemistry in a classroom. The two metrics used to measure ozone reactivity with the occupants were the ozone decay rate (κ_p) and deposition velocity ($v_{d,p}$). The value for κ_p was determined by first calculating the occupied classroom air exchange rate (AER) and the total ozone decay rate, κ, to the space. The AER can be estimated during occupied periods by doing a steady-state mass balance on the CO_2 concentration by assuming a certain CO_2 emission rate from the occupants within the portable classroom. With this AER, κ can be calculated from a steady-state mass balance on ozone using the measured indoor and outdoor ozone concentrations during the same period over which the AER was calculated. The value of κ is a summation of κ_p and the ozone decay rate to building materials, κ_b when the classroom is occupied. During unoccupied times, tests were performed in the same portable classrooms to determine κ, because without occupants, $\kappa = \kappa_b$. Before κ can be calculated, the AER during unoccupied periods is determined by performing a CO_2 decay test. Carbon dioxide is released into a space up to a concentration in excess of 2000 ppm and monitored until the concentration decreases to a few hundred ppm greater than ambient (≈400 ppm). The AER is determined iteratively by comparing the measured CO_2 concentrations with those calculated from a dynamic mass balance on CO_2 assuming some value for the AER. The AER is varied until a minimum least-squares difference between the measured and calculated CO_2

concentrations has been found. In a similar manner, κ_b during unoccupied times is determined by performing an ozone decay test. In this instance, the same procedure is performed as with the CO_2 decay test, except the κ_b term is manipulated in the dynamic mass balance to minimize the least-squares difference. With κ_b known, κ_p can be calculated by $\kappa - \kappa_b$. From this, $v_{d,p}$ can be calculated by multiplying κ_p by the volume of the space and dividing by a person's body surface area (BSA). Equations 1 and 2 refer to the steady-state and dynamic mass balances, respectively, used to determine κ.

$$C_{SS} = \frac{pC_O + \frac{E}{\lambda V}}{1 + \frac{\kappa}{\lambda}} \tag{1}$$

$$C_t = C_{t=0}e^{\beta t} + \left(p\frac{\lambda}{\beta}C_0 + \frac{E}{\beta V}\right)\left(1 - e^{-\beta t}\right) \tag{2}$$

where:

C_{SS} = steady-state concentration of CO_2 (ppm) or O_3 (ppb)

C_0 = outdoor concentration of CO_2 (ppm) or O_3 (ppb)

p = penetration factor (%)

E = emission rate of CO_2 (ppm/h) or O_3 (ppb/h)

κ = total ozone decay rate (h^{-1})

λ = air exchange rate (h^{-1})

V = volume of the room (m^3)

C_t = dynamic concentration of CO_2 (ppm) or O_3 (ppb)

$C_{t=0}$ = initial concentration of CO_2 (ppm) or O_3 (ppb)

β = $\lambda + \kappa$ (h^{-1})

Effects of Scented Body Sprays on Ozone Reactivity with Building Occupants

The effects of scented body sprays on $v_{d,p}$ were tested in an 11 m^3 stainless steel chamber at the University of Texas at Austin's J. J. Pickle Research Campus. The chamber was outfitted with a duct system that pulled air from the laboratory, measured the flow rate, injected ozone into the air stream, and supplied air to the chamber. Ozone concentrations were measured at the outlet of the duct and in the center of the chamber at 1-second intervals, but 3-minute averaged concentrations were used to reduce the variability in measurements.

Ozone was supplied at a constant rate to the chamber at a certain AER until an approximate steady-state concentration was reached. At this point, a human subject would enter and remain in the chamber until the difference between the 3-minute averaged ozone concentrations measured in the center of the chamber was less than 2 ppb. The subject then exited the chamber and a body spray was applied to their upper torso. Only one commonly occurring body spray was used for testing based on a composition analysis performed on five different body sprays. The body spray that had the highest percent by mass of linalool was chosen because linalool and ozone are known to react at favorable rates (Bernard et al., 2012) compared to other compounds in the body spray of a similar magnitude. The subject re-entered the chamber and remained inside again until the difference in 3-minute averaged ozone concentrations was sufficiently small.

The κ values were calculated using Eq. 1. Values for κ_b and κ can be calculated directly by comparing the ozone concentrations measured at the outlet (C_0 in Eq. 1) and in the center of the chamber (C_{SS} in Eq. 1) during unoccupied and occupied periods, respectively. The CO_2 decay tests were unnecessary because the AER was measured directly by the flow meter within the duct. Once κ_p was determined, $v_{d,p}$ was calculated

using the subjects' BSAs and chamber volume. The height and weight of both subjects was known so their BSA was calculated according to the Du Bois formula given by:

$$BSA = 0.0007185W^{0.425}H^{0.725} \tag{3}$$

where W is the subject's mass (kg) and H their height (cm). With this value, $v_{d,p}$ for each subject was calculated and compared to previous experiments following the same procedure outline in this section but using three T-shirts instead of human subjects.

Major Findings and Conclusions

Ozone Decay Rate and Deposition Velocity to Students in Portable Classrooms

The indoor CO_2 and ozone dynamics during a spring day in one of the portable classrooms is illustrated in Figure 1. Periods with elevated CO_2 concentrations indicate students are occupying the room. During these same periods, but with a few minute lag, the ozone concentration begins to decrease because ozone has started reacting with the skin oils on students. One can get a general sense of the occupancy dynamics throughout the school day based on the CO_2 concentrations. Initially, the room is unoccupied at 9:00 am and then students begin to enter as the CO_2 concentrations begin to increase while ozone levels decrease to the instrument's detection limit. The decrease in CO_2 concentration and subsequent increase in ozone concentration indicates a passing period from about 10:30 am to 10:45 am. From 10:45 am to 12:30 pm, the CO_2 concentration increases but does not reach the same concentration as earlier indicating less students are in the room for this class period. At about 12:30 pm, the students leave and the indoor ozone rises rapidly to an I/O ratio of about 0.7. During this same period, the CO_2 concentration returns to nearly outdoor levels, indicating a high AER. When students start to enter around 2:45 pm, the CO_2 concentration increases dramatically to near the instrument's upper detection limit while the ozone declines to its instruments lower detection limit.

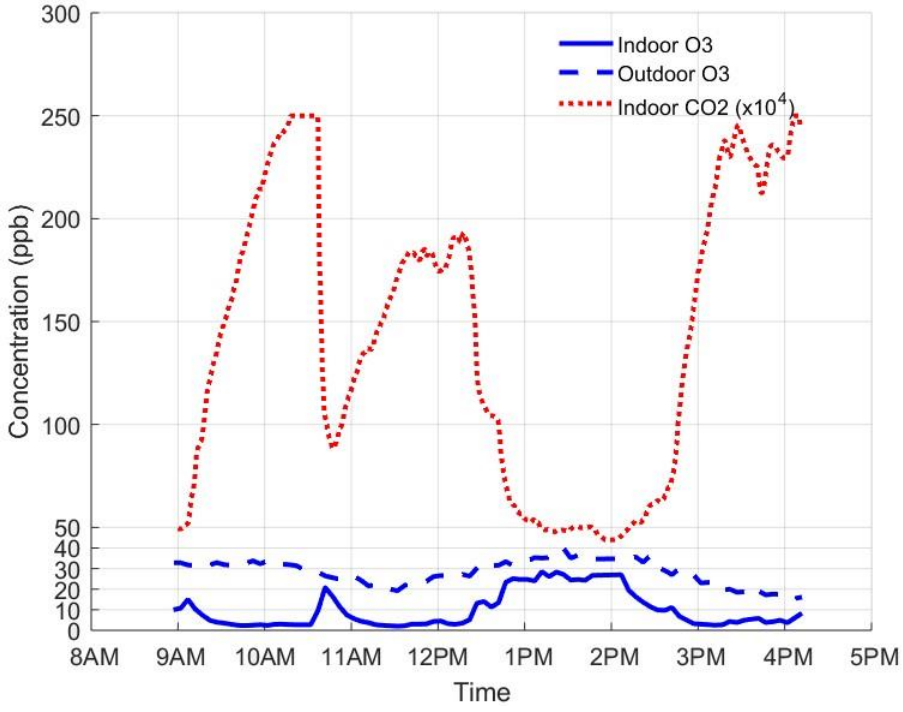


Figure 1: Example of measured CO_2 and indoor and outdoor ozone concentrations in a portable classroom during Spring 2016

The calculated ozone decay rates are shown in Figure 2. Results are relatively consistent barring classroom 5. The values for κ and κ_b for classroom 5 are based on only one period's CO_2 and ozone measurements whereas the values for the remaining classrooms are made up of 3 to 16 periods of measurements. Therefore the κ and κ_b for classroom 5 could be misrepresented.

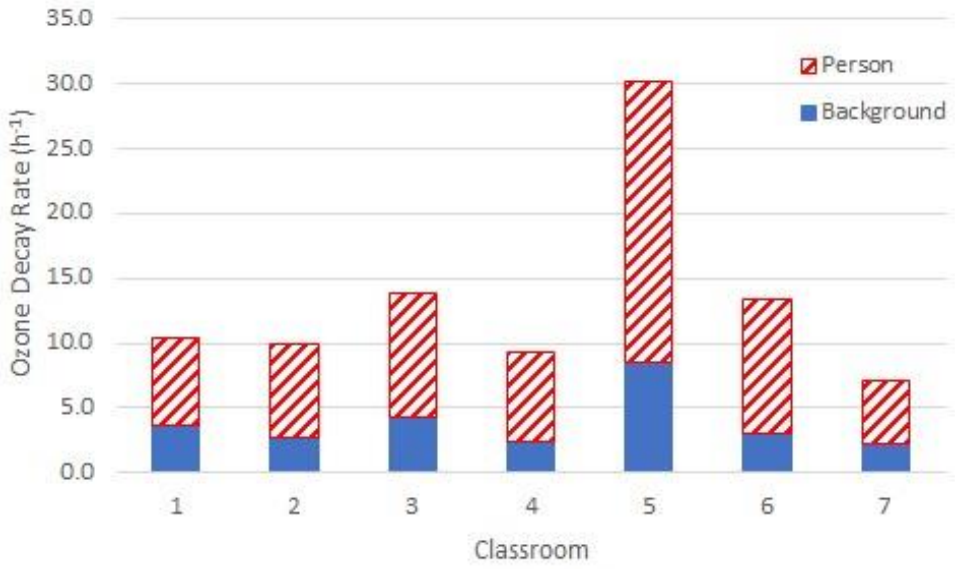


Figure 2: Ozone decay rate attributed to surface reactions, κ_b, and reactions between ozone and compounds on a single student's skin and clothing, κ_p. On average, the ratio of the ozone decay rate with people to that with surfaces is 2.8:1.

The average value of $v_{d,p}$ for each portable classroom was obtained by multiplying the values of the hashed portions in Figure 2 by the volume of the respective classroom and dividing by an averaged BSA of high school aged males and females. These values are shown in Figure 3. The average $v_{d,p}$ for classroom 5 is high since κ_p is large and the volume to surface area ratio for each classroom is relatively similar. Barring classroom 5, the results from this study are near the upper $v_{d,p}$ values found elsewhere in the literature. Fadeyi (2015) summarized a majority of studies using field data, chamber experiments, and computational fluid dynamics (CFD) models to calculate $v_{d,p}$ and report a range of values between 5.4 m/h to 22.3 m/h. Average $v_{d,p}$ values in this study fall in the upper half of this range or above and might be attributed to the difference in AERs. Most studies consider AERs in the range 0.5 to 1 h^{-1} (Rim et al., 2009; Wisthaler and Weschler, 2010; Yang et al., 2016), but AERs measured in the portable classrooms ranged from 0.7 to 4.8

h^{-1}. A larger AER means there will be an increase in turbulent kinetic energy (TKE) within the space, allowing ozone molecules to interact more often with human and material surfaces. Greater TKE in addition to the high occupancy density in the portable classrooms could explain why $v_{d,p}$ values in this study are so high. Another hypothesis is that the perfumes, colognes, and air fresheners noted during data collection could be emitting reactive terpenes and terpene-related species to the portable classroom space increasing ozone chemistry.

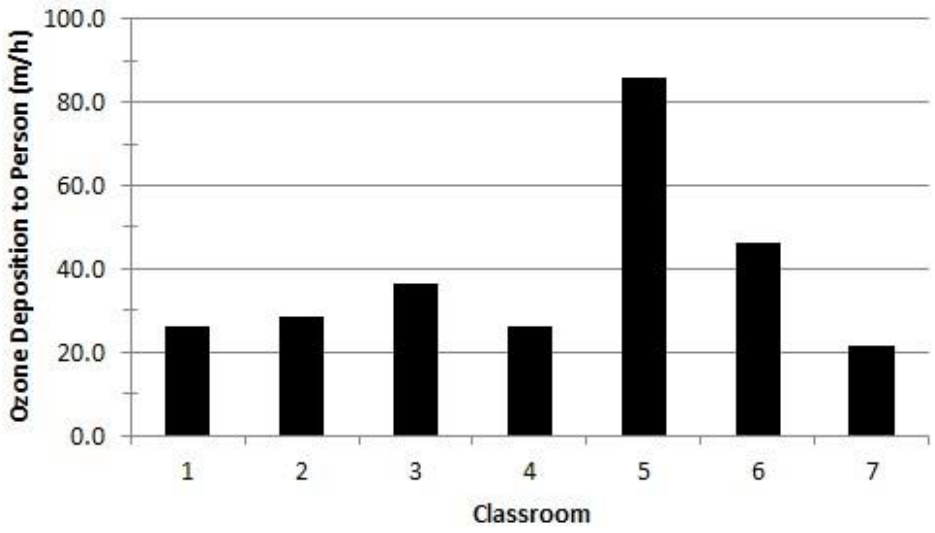


Figure 3: Ozone deposition velocities to a single student's skin and clothing, κ_p, for each of the portable classrooms

EFFECTS OF PERSONAL CARE PRODUCTS ON OZONE REACTIVITY

An example of the ozone concentration for a chamber experiment with a human subject is shown in Figure 4. During the first occupied period, the subject was wearing an old t-shirt and jeans with no body spray. During the second occupied period, a mass of 1.2 g of the body spray had been applied. Periods when the doors were opened to allow occupants to exit the chamber are shown because ozone concentrations decreased due to

dilution by laboratory air. A similar phenomenon occurred when doors were opened to allow the subject to enter the chamber, but the decrease in ozone concentration from dilution is negligible compared to the contribution from reactions with the subjects. Additionally, any decrease in ozone concentration by dilution would be negligible after running the experiment for at least 30 minutes. Occupied times ranged from 30 to 54 minutes and all but one experiment were conducted at an AER of 4 h^{-1}.

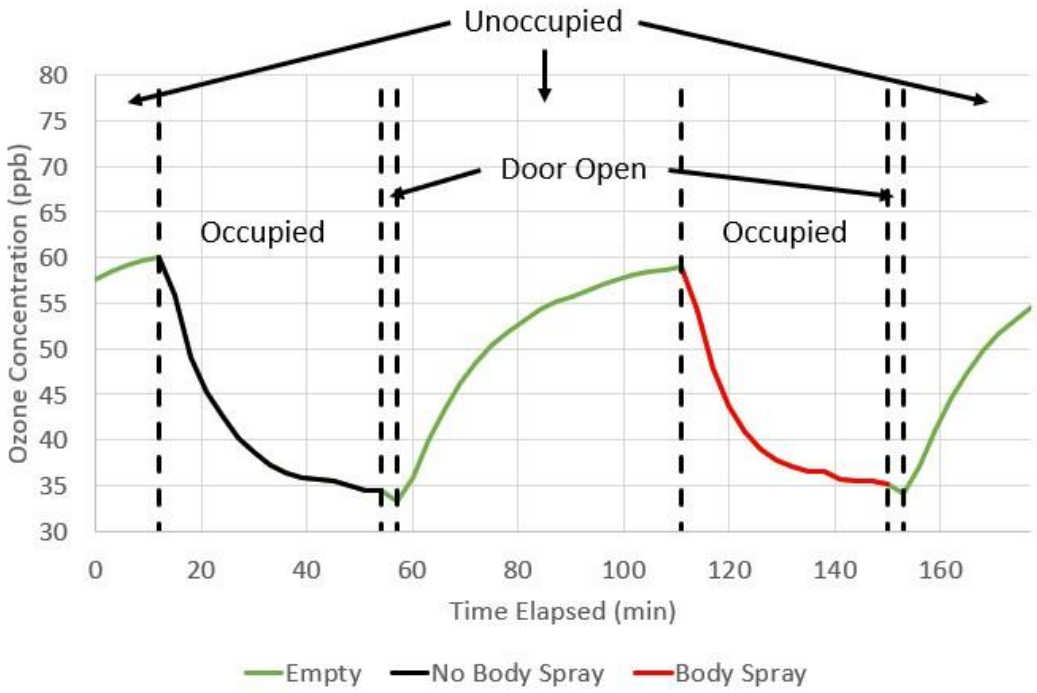
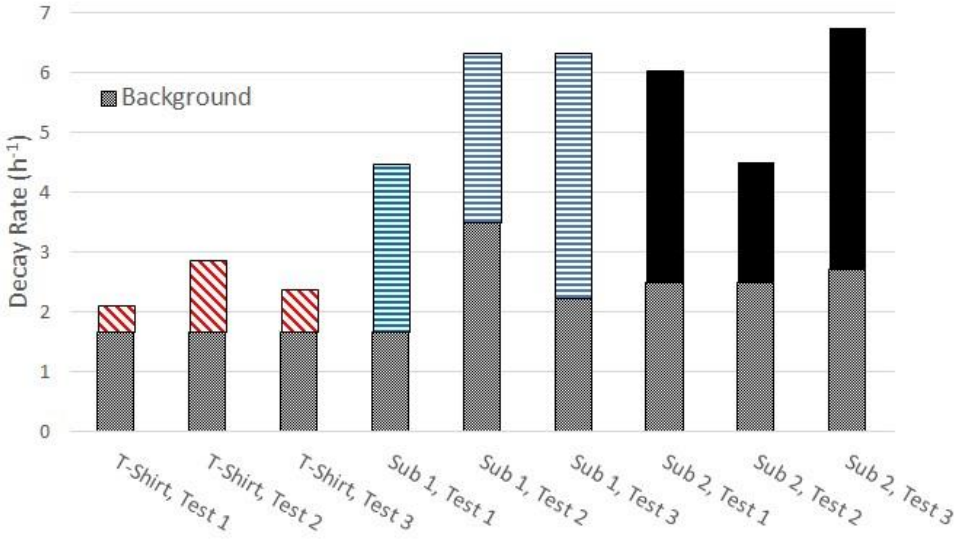


Figure 4: Example ozone concentration profile during single occupant experiment

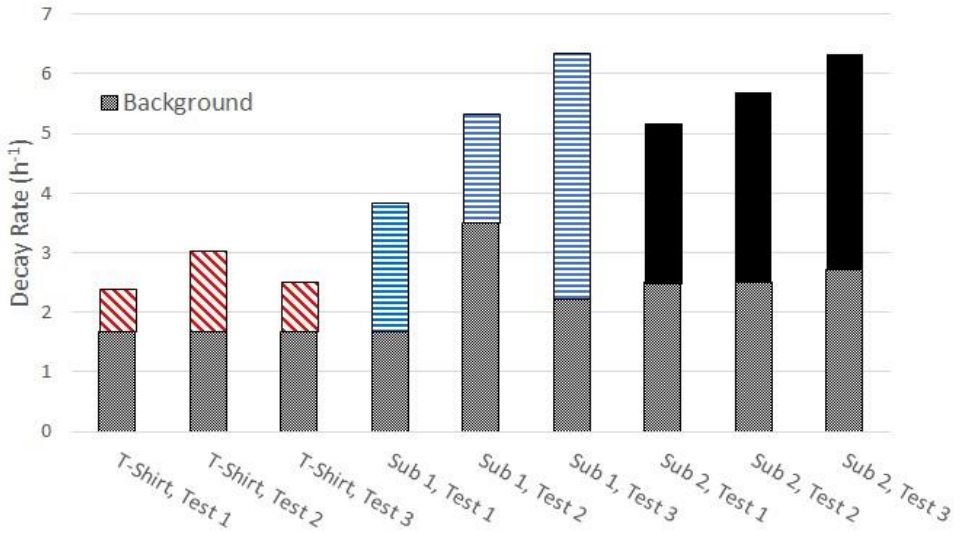
Six total experiments were executed with human subjects (3 for each subject) and three experiments were conducted using T-shirts without and with the body spray applied. Ozone decay rates for every trial are shown in Figure 5. Both subjects had an average κ_p of 3.2 h^{-1} without the body spray applied. In a similar study to the trials performed without a body spray applied, Wisthaler and Weschler (2010) reported κ_p values for two people in an

office-sized chamber ventilated with an AER of 1 h^{-1} of 1.7 h^{-1} and 2.0 h^{-1} in two separate scenarios. Rim et al. (2009) determined similar values for κ_p between 1.35 to 1.62 h^{-1} when simulating a human body and heat output in a computational fluid dynamics (CFD) model using AERs between 0.71 and 0.86 h^{-1}. Results from this study show that humans are potentially more reactive than others have reported, even without application of a body spray. When the body spray was applied, the average κ_p values were 2.7 h^{-1} and 3.2 h^{-1} for Subject 1 and Subject 2, respectively.

Comparisons between the average $v_{d,p}$ calculated for each subject and the T-shirt experiments without and with the body spray applied are shown in Figure 6. Without the body spray applied, the average $v_{d,p}$ to Subject 1 was 17.0 m/h and to Subject 2 was 15.3 m/h. These values fall within the range reported by Fadeyi (2015). Wisthaler and Weschler (2010) measured $v_{d,p}$ values of 14.4 m/h and 18 m/h in a simulated office environment ventilated at 1 h^{-1}. Fadeyi et al. (2013) also modeled their chamber to represent a typical office space and found that, at a ventilation rate of 1 h^{-1}, $v_{d,p}$ ranged between 14.4 and 22.3 m/h. Yang et al. (2016) extracted skin oil from worn clothing and exposed it to ozone in a chamber ventilated with an AER of 1 h^{-1} and calculated an ozone deposition velocity of 5.4 m/h.



(a) No body spray applied



(b) Body spray applied

Figure 5: Comparison of background to per person or cotton T-shirt ozone decay rates. The height of the bar represents the total ozone decay rate, κ; the bottom portion represents decay just to background surfaces, κ_b; and the remainder is the decay rate to a single occupant, κ_p, or T-shirt, κ_c

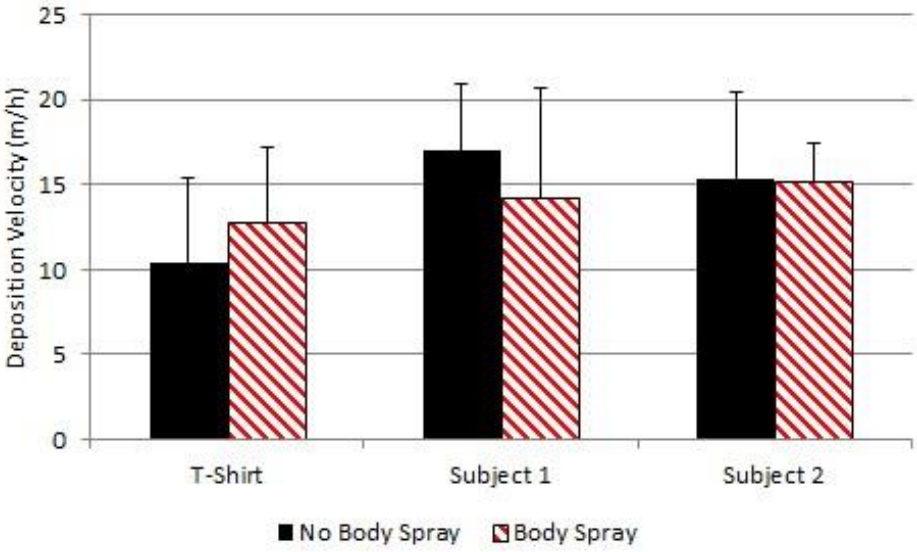


Figure 6: Average deposition velocities without and with the body spray applied from the T-shirt experiments and those with Subject 1 and Subject 2

Average $v_{d,p}$ when occupants wore body sprays were 14.2 m/h and 15.2 m/h for Subjects 1 and 2, respectively. Based on these results, and the values for κ_p in Figure 5, application of the body spray does not increase the ozone reactivity to and around building occupants. The data shown in Figure 6 indicate that, on average, the subjects tended to be less reactive when the body spray was applied. However, the difference is not significant. Differences could easily be a result of uncertainties in ozone measurements, variations in the amount of ozone generated within the supply duct, or fluctuations in the ozone concentration within the general laboratory.

Nevertheless, decreased reactivity could be possible due to competing reactions between ozone and reactants in the body spray and between ozone and human skin lipids. Corsi et al. (2007) found that linalool concentrations at its odor threshold, approximately 1000 ppb, reduced the ozone concentration by only 1%. Based on the amount of body spray applied and the percent by mass of linalool, the maximum linalool concentration in the

chamber would have been approximately 1100 ppb. Assuming this concentration remained constant during the experiment, gas-phase reactions between ozone and linalool would only account for 1% of the decrease in ozone concentration. However, surface reactions between ozone and sorbed terpenes may account for a larger fraction of the ozone uptake. Shu and Morrison (2012) found that 95% of the reactions between ozone and DHM occur on surfaces and surface-specific ozone reaction probabilities for d-limonene are 10 to 100 times greater than those in the gas-phase (Springs et al., 2011). Even though compounds are continuously emitted after applying the body spray, reactions in the gas phase might not effectively alter ozone concentrations near building occupants. According to Weschler (2000), the half-life for d-limonene, one of the more reactive terpenes, concentrations in the presence of ozone is about 0.75 hours. An AER of 4 h^{-1} means that the air will be recycled every 0.25 hours, on average, and that reactions between compounds like d-limonene and ozone will not have a large effect on the bulk ozone concentration.

The lack of gas-phase chemistry means surface reactions between reactive molecules on human/clothing surfaces and ozone represent the largest potential sink for indoor ozone. Applying a body spray adds to the number of reactive compounds present on human surfaces, but reactions between ozone and human skin tend toward being transport-limited (Rim et al., 2018). This fact means that the frequency with which ozone interacts with compounds on human surfaces is the limiting factor in the reactions between humans and ozone, not the concentration of reactive species on human skin surfaces. Additionally, ozone uptake might be reduced due to steric hindrance of the body spray's primary constituent, DHM. Research has shown that DHM molecules might fold over when sorbed to surfaces, effectively covering the carbon-carbon double bond that ozone reacts with so favorably (Forester et al., 2006; Ham and Wells, 2009). Therefore, ozone is primarily reacting with skin lipids rather than the compounds from the body spray sorbed

to the subject's skin and clothing. This means that surface reactions on human skin are not going to be significantly higher with the body spray applied versus without. It is even plausible that DHM in body sprays shields squalene and other reactive compounds in skin lipids, thereby slightly decreasing the reactivity of building occupants who wear such body sprays.

The body spray used in this study does not seem to effectively alter the ozone chemistry near and on human skin surfaces based on the calculated $v_{d,p}$. Measurements of reactive VOCs (DHM and linalool) during experiments with human subjects following application of a body spray indicate that ozone chemistry occurred, but that concentrations of reactive species emitted from the applied body spray were too low to exert a measurable change in ozone concentration in chamber air. Despite this finding, near-head chemistry may still be important in terms of the production sensory irritants. Additional personal care products, such as deodorants or colognes/perfumes, with different chemical compositions should be tested to ascertain how these products differ from the one tested in this study, and to determine their effects on indoor ozone concentrations. Future studies should also consider the effects of AER on ozone uptake to building occupants without and with these different personal care products and how air flow around a human subject might alter the types and concentrations of by-products generated from reactions between ozone and terpenes found in scented personal care products.

Appendix A: Journal Article under Development—Effects of Scented Personal Care Products on Ozone Reactivity with Building Occupants

ABSTRACT

Ozone enters building spaces through infiltration, and natural and mechanical ventilation. Ozone is a respiratory irritant and known asthmagen, and some of the by-products from ozone reactions with volatile organic compounds (VOCs) and indoor materials can be irritating or worse. One widely studied ozone-VOC reaction involves terpenes and terpene alcohols, unsaturated compounds that are readily found in cleaning products, air fresheners, body sprays, and deodorants because of their pleasant-smelling fragrances. Terpenes, along with molecules present on indoor furnishings and human skin lipids, represent sinks for indoor ozone. In this study, the terpene compositions of several common male body sprays are characterized. One particular body spray was selected for experimental analysis based on the concentration of terpene alcohols in the product. The body spray's effects on the ozone deposition velocity to cotton clothing and human subjects were tested in a stainless steel environmental chamber. The average ozone deposition velocity to humans without the body spray applied was found to be 16.2 m/s. When the body spray was applied, the average deposition velocity decreased to 14.7 m/s. The results of this study suggest that at least some scented body sprays might not noticeably alter the ozone reactivity of clothing or a person. However, results also indicate that building occupants might be more reactive in the presence of ozone than previous studies have found, particularly under elevated mixing conditions in the interior space.

INTRODUCTION

Just over one-third of the Americans live in cities classified as ozone "non-attainment areas" by the USEPA. The eight-hour National Ambient Air Quality Standard

(NAAQS) for ozone was most recently revised in 2012 and sets a limit of 70 ppb over an 8-hour exposure period (EPA, 2015 and 2018). Recent studies have found that many sites in the south central United States are unable to meet the 2012 NAAQS for ozone (Sather and Cavender, 2012; Sather and Cavender, 2016).

Elevated ozone concentrations have been linked to increased hospitalization rates, especially among the young and elderly (Burnett et al., 2001; Yang et al., 2003; Ji et al., 2011). Multiple studies have shown correlations between short-term increases in ground-level ozone concentrations and increased mortality (Bell et al., 2005; Zanobetti and Schwartz, 2008; Jerrett et al., 2009; Di et al., 2017a). Chronic exposures to ozone concentrations between 10 and 100 ppb have been shown to reduce the function of small airways (Tager et al., 2005) and have been associated with the onset of asthma (McConnell et al., 2002), cardiovascular disease (Bell et al., 2004; Goudarzi et al., 2013), and chronic obstructive pulmonary disease (Burnett et al., 1997; Khaniabadi et al., 2017). The main symptoms associated with acute exposure to elevated ozone concentrations include inflammation of respiratory tissue (Triche et al., 2006) and aggravated asthma (Kim et al., 2011; Sousa et al., 2013).

Ozone is transported into buildings from outdoors through mechanical and natural ventilation, as well as infiltration. The ratio of indoor ozone concentrations to those outdoors (I/O) are commonly between 0.2 and 0.7 for homes (Weschler, 2000), with values less than 0.2 in more recently-constructed residential buildings (Lee et al., 2002; Lee et al., 2004). The I/O ratio is also heavily dependent on the type of ventilation strategy used (Walker and Sherman, 2013), and particularly the magnitude of the air exchange rate (AER) between outdoors and indoors. Homes that rely on natural ventilation generally have higher I/O ratios, while those with air conditioning units and filters will have lower I/O ratios (Stephens et al., 2011; Walker and Sherman, 2013).

Indoor sources of ozone also exist. Ozone can be emitted from commercial ozone-generating air purifiers (Boeniger, 1995; Hubbard et al., 2005; Mang et al., 2009), ionizing portable air purifiers (Waring et al., 2008; Kim et al., 2017), electrostatic precipitators (Poppendieck et al., 2014; Xiang et al., 2016), and office equipment such as photocopiers (Black and Worthan, 1999; Destaillats et al., 2008; Wang et al., 2012; Vicente et al., 2017). Even with these sources, the indoor ozone concentration tends to be lower relative to outdoors, primarily because of ozone's reactivity with building materials (Grøntoft and Raychaudhuri, 2004; Gall et al., 2013; Rim et al., 2016), furnishings (Lee et al., 1999; Morrison and Nazaroff, 2000; Kruza et al., 2017), and human skin lipids (Wisthaler and Weschler, 2010; Rim et al., 2018).

Ozonolysis of commonly occurring indoor volatile organic compounds (VOCs) has been well-studied (Bailey, 1958; Johnson and Marston, 2008; Waring and Wells, 2015; Ridgway et al., 2017). One important class of VOCs are terpenes and terpene alcohols, which are used in a wide variety of consumer products (Sarwar et al., 2004; Nazaroff and Weschler, 2004; Steinemann, 2015). Terpenes are used in cleaning agents (Shin et al., 2016; Nørgaard et al., 2014a) as natural or "green" ingredients, and in air fresheners (Vu et al., 2013; Kim et al., 2015). Terpene-ozone reaction chemistry has been actively studied over the past 20 years (Nazaroff and Weschler, 2004; Destaillats et al., 2006; Singer et al., 2006a; Sarwar and Corsi, 2007; Coleman et al., 2008b; Nørgaard et al., 2014b; Youssefi and Waring, 2015), and now attention is shifting toward terpene-ozone reactions associated with personal care products (P_eCPs), including lotions and scented body sprays. Corsi et al. (2007) completed a screening assessment and hypothesized that humans wearing scented P_eCPs generate a "personal reactive cloud" that might influence ozone oxidation chemistry in the wearer's breathing zone.

Some of the more stable by-products generated by ozone-terpene reactions include aldehydes, ketones, and organic acids (Weschler, 2000; Destaillats et al., 2006; Rohr, 2013). These by-products can be more harmful or irritating than the terpene precursors. Ozone reactions with d-limonene, a common indoor terpene, have been found to generate by-products that act as dermal allergens (Clausen et al., 2001), eye irritants (Klenø and Wolkoff, 2004; Nøjgaard et al., 2005), and known carcinogens such as formaldehyde (Weschler, 2006; Salthammer et al., 2010). Oxidation products of α-pinene, another common indoor terpene, have been shown to reduce airflow and produce sensory irritants (Rohr et al., 2002) in addition to reactive oxygen species that can harm biological tissue (Venkatachari and Hopke, 2008). Secondary organic aerosols (SOA) are also generated from terpene-ozone reactions (Sarwar and Corsi, 2007; Ito and Harashima, 2008; Chen et al., 2010; Huang et al., 2011; Youssefi and Waring, 2012) that contribute to the particulate matter loading in a building. SOA exposure has been linked to symptoms such as increased pulmonary inflammation (Rohr, 2013; Niu et al., 2017)

Terpenes in air and on surfaces represent important sinks for indoor ozone (Grøntoft and Raychaudhuri, 2004; Tama´s et al., 2006), but arguably the most important reaction site in densely populated spaces is the skin of human occupants. Human skin oil contains unsaturated organic species that can appreciably reduce the ozone concentration in a room. Previous studies have shown that exposing humans or soiled clothing in enclosed spaces to ozone will markedly reduce the ozone concentration (Coleman et al., 2008a; Wisthaler and Weschler, 2010; Rai et al., 2013; Gao et al., 2015). Squalene represents about 25% of the lipids present on human skin and is highly reactive with ozone (Weschler, 2000; Wang et al., 2015; Tang et al., 2016). Squalene is a low volatility compound that contains six unsaturated carbon-carbon bonds that when reacted with ozone leads to the production of acetone, 4-oxopentanal (4-OPA), and 6-methyl-5-hepten-2-one (6-MHO) as

by-products (Wisthaler and Weschler, 2010; Yang et al., 2016). Ozone reactivity to humans in buildings can be anywhere from a few times to an order of magnitude greater than to typical indoor materials (Grøntoft and Raychaudhuri, 2004; Wisthaler and Weschler, 2010; Fischer et al., 2013).

This study aims to characterize the chemical composition of common body sprays and to further examine the effects of one of these body sprays on ozone reactions with cotton clothing and two adult males. The decrease in ozone concentration inside a stainless steel environmental chamber is quantified after ozone is given time to react with cotton T-shirts and later with a single human subject with and without a body spray having been applied. The objective of this research was to ascertain whether or not application of a body spray on clothing and occupants increases the ozone deposition velocity, thus making the wearer more reactive.

METHODOLOGY

This research involved a composition analysis of five common male body sprays, and the analysis of the effects of one of these sprays on ozone removal to unworn T-shirts, as well as two human subjects.

Product Characterization

There are many types of body sprays available on the market today. Rather than characterize, apply, and analyze a majority of these products, one particular brand of body spray was focused on. This brand has multiple products, so the composition of each was assessed using small test chambers. Individual products were sprayed onto an 11 cm by 21 cm Kimwipe® for approximately two seconds. The Kimwipe was then attached to a stainless steel frame and sealed in a 10-L stainless steel sample chamber outfitted with two

6.4 mm Swagelok® bulkhead union fittings. A stainless steel tee was attached to one of the bulkhead unions and a Swagelok needle valve was attached to one side of the tee.

Chamber air samples were collected on sorbent tubes. A sorbent tube was inserted into a one centimeter length piece of I.D. 6.4 mm Teflon® tubing and attached to the other branch of the tee. All sorbent tubes consisted of a 3 mm I.D. tapered GC focus liner with frit (Optic 2/3 Injector System) packed with approximately 75 mg of 80-100 mesh Tenax TA®. The inlet of a 2 L/min sample pump was attached to the bulkhead union supporting the sorbent tube and needle valve and the outlet attached to the other bulkhead union. The pump recirculated the air from the chamber through the sorbent tube for approximately 45 minutes. The needle valve was used as a bypass to control the air flow rate. A nominal flow rate of 20 mL/min was used for each sampling event. Flow rates were measured using a bubble flow meter (Sensidyne, Gilian Gilibrator™).

The VOCs collected on sorbent tubes were analyzed using zero-path thermal desorption followed by gas chromatography and mass spectrometry as described in Section 2.3. Individual VOCs were identified using the Library Compound Search (LCS) function of ChemStation™ software. The relative mass of the identified compounds was calculated using the internal standard with an assumed relative response factor of one. The selected body spray used in the application stages consisted primarily of dihydromyrcenol (DHM) and linalool, also primary components of the other body sprays that were tested.

Configuration of the Controlled Environmental Chamber

The environmental chamber had a volume of 11 m^3 with inside walls made of stainless steel. Air from the lab space was conveyed under positive pressure into a 20 cm diameter duct that extended into the center of the chamber, elbowed 90° toward the wall opposite the entrance, and tapered to a diameter of 10 cm. The outlet from the duct was

placed 10 cm from the wall to create an impinging jet to help induce mixing. Ozone was generated within the duct by a small ozone generator (Ozotech, Poseidon Ozone Generator). The ozone was released into the chamber where two small fans (Startech, 80x25 mm ball bearing) were used for purposes of mixing. The ozone concentration was measured just inside the outlet and in the center of the chamber by vinyl tubing connected to two ozone monitors (HORIBA, APOA-370) placed outside the chamber.

The chamber employs a two-fan system where one fan supplies air from the laboratory into the chamber and another pulls the air from the chamber into the exhaust. A flowmeter (EBTRON, GTx116-P+) in the duct allows determination of the chamber air exchange rate (AER). Before introducing clothing or a subject into the chamber, the fan system was turned on and adjusted to the correct settings. Once set, the ozone generator, ozone monitors, pump, and inner-chamber fans were turned on. The system was left to run for at least $3/\lambda$ hours, where λ is the AER (h^{-1}), to allow for an approximate steady-state ozone concentration. The concentrations within the chamber and at the outlet of the duct were monitored over this period to ensure that the ozone concentration did not vary substantially.

Product Application to Clothing

A series of three experiments were conducted on three, once-laundered T-shirts before testing commenced on human subjects. The T-shirts were each medium-sized, white, and purchased in a pack of nine. The T-shirts were laundered once together using an unscented laundry detergent in a cold-wash cycle followed by a normal drying cycle.

After the ozone concentration in the chamber reached a stable concentration, two T-shirts on wire hangars were hung in the middle of the chamber and the third laid over the back of a wooden chair placed just off-center. Ozone reacted with the T-shirts until a

new steady-state was achieved. The T-shirts were then removed until the original steady-state ozone concentration was re-established in the chamber. A body spray was applied to the front and back of each T-shirt in a separate laboratory and then quickly (within 1 minute) placed back in the chamber according to the same set-up described earlier. The body spray canister was weighed before and after application to determine the mass applied. Again, the ozone concentration within the chamber was monitored and the T-shirts were removed once a new steady-state ozone concentration was reached. Two more experiments using the remaining T-shirts were conducted according to the same procedure.

Product Application to Human Subjects

Trials with human subjects were conducted in a similar manner to those with T-shirts. The chamber system was turned on and left until a steady-state ozone concentration was established. A human subject, dressed in recently cleaned but old T-shirt and jeans, entered the chamber and remained inside until a new, steady-state ozone concentration was achieved. The subject then exited so that the initial ozone concentration was re-established. The subject was then taken to a separate laboratory where the body spray was applied to the front of the subject's upper torso. The subject then re-entered the chamber within 30 seconds after application of the body spray. Once a new steady-state ozone concentration was achieved or the difference between 3-minute averaged ozone concentrations was less than 2 ppb, the subject exited the chamber and the system was left to return to its initial state. These experiments were conducted a total of six times - three times with one subject and then three times with a different subject. Subjects did not use any scented colognes or other P_eCPs prior to the experiment.

Chamber VOC Sampling Procedure and Analysis

Volatile organic compound samples were collected during the experiments involving human subjects both with and without the body spray applied. Using a sampling system consisting of a sorbent tube, Teflon tubing downstream of the sorbent tube, and a Buck® sample pump, VOC samples were collected for periods when a human subject occupied the chamber. The flow rate was measured using a bubble flow meter (Sensydine, Gilian Gilibrator™) and the nominal sampling rate was 20 mL/min. Sample collection was initiated when the collection system was placed in the test chamber by the subject and continued until the ozone concentration in the chamber stabilized. Collection times varied from approximately 28 to 45 minutes.

Analysis of VOC samples was completed using a Hewlett-Packard® (HP) gas chromatograph (GC) model number 5890 II outfitted with a HP 5971 mass selective detector (MS). The analytical column was a 30 m long Restek Rxi624 Sil MS with an internal diameter of 0.25 mm supporting a 1.4-micron film (serial number 1059060). Samples were injected directly onto the column using a zero-pathway Atas Optic II Thermal Desorption Unit (TDU).

The temperature profile for the GC oven started with a two minute hold at 40°C followed by a temperature ramp of 8 C/min to a temperature of 75°C, and then a temperature ramp of 20°C/min to a final temperature of 280°C. The Atas TDU method employed an initial temperature of 50°C followed by a 10°C/s temperature ramp to a final temperature of 280°C. The helium carrier gas through the TDU began with an initial transfer pressure of 10 psi. After two minutes, the carrier pressure was reduced to 7 psig, producing an analytical flow rate of approximately 1 mL/min through the column. To maintain a 1 mL/min flow rate, the carrier gas pressure was linearly increased to a final pressure of 25 psig.

The mass of DHM and linalool that was collected during each experiment was determined using a five-point calibration curve using 1-bromo-4-fluorobenzene (Sigma-Aldrich 99%) as an internal standard. The values determined from this test correspond to the average masses of DHM and linalool during the length of the experiment.

Data Analysis

The main parameters estimated in these sets of experiments were the ozone decay rate and deposition velocity.

Decay Rate

The ozone decay rate, κ, was determined by rearranging the general, steady-state mass balance equation for a single compartment with no indoor emission sources:

$$\kappa = \lambda\left(\frac{C_{out}}{C} - 1\right) \tag{4}$$

Where, λ is the AER measured in the chamber (h^{-1}), C is the ozone concentration in chamber air (ppb), and C_{out} is the ozone concentration in the supply air (ppb). Solving Eq. 4 gives the total κ for the chamber. During occupied periods, κ is the sum of the decay rate to background surfaces, κ_b, and to T-shirts (κ_c) or occupants (κ_p). For unoccupied periods, $\kappa_b = \kappa$, which allows κ_p to be determined during occupied periods as $\kappa - \kappa_b$.

Deposition Velocity

The deposition velocity was calculated by:

$$v_d = \kappa\frac{V_C}{A} \tag{5}$$

Where, v_d is the deposition velocity (m/h), V_c is the volume of the test chamber (m^3), and A is the surface area of the material removing the pollutant (m^2). The deposition velocity is related to the surface removal of ozone and is incorporated into a mass balance by multiply by the surface area and the concentration in the indoor space to get units of mass per time. The deposition velocity is also defined as:

$$\frac{1}{v_d} = \frac{1}{v_t} + \frac{4}{\gamma \langle v_b \rangle} \tag{6}$$

Where v_t is the transport-limited deposition velocity (m/h), γ is a reaction probability, and $\langle v_b \rangle$ is the Boltzman velocity (3.62×10^4 cm/s for O_3 at 296 K). The value for v_t is always greater than that of v_d because v_t represents the maximum mass transfer coefficient given a certain flow condition. For cases when v_t is much greater than v_d, γ is only a function of v_d and $\langle v_b \rangle$, which means that slow surface reactivity governs the overall uptake of ozone.

RESULTS AND DISCUSSION

Terpene Composition of Body Sprays

A summary of the results from the characterization of five common body sprays are presented in Table 1. Spray 2 was chosen for application in the experimental phase because it contained a high concentration of DHM and the highest concentration of linalool. Between DHM and linalool, linalool has a greater reaction rate with ozone (Mallard et al., 1998). Other common terpenes found in body sprays are also included in Table 1 as a reference. Other terpene compounds and several dozen non-reactive ingredients were also identified and approximately quantified for each body spray. These

compounds and their percentage by mass in the body spray are provided in Tables 5 through 9 in Appendix B.

Table 1: Percent by mass of common terpene and terpene alcohols in body sprays tested

Compound	**Spray 1**	**Spray 2**	**Spray 3**	**Spray 4**	**Spray 5**
Dihydromyrcenol	7.2	20.1	22.0	23.5	7.4
Linalool	1.1	5.9	4.6	4.9	3.5
Geranyl Acetate	0.3	0.2	-	-	0.3
α-Pinene	0.1	0.2	-	0.1	0.2
d-Limonene	0.1	-	0.4	0.1	-

Dihydromyrcenol is a naturally occurring monoterpene alcohol used widely in products like soaps, detergents, body sprays, general purpose cleaners, and other household products (Nazaroff and Weschler, 2004; Singer et al., 2006b; Nørgaard et al., 2014a). While not as reactive as other monoterpenes like d-limonene, DHM on surfaces, especially at the concentrations found in the body sprays, represent potentially appreciable sinks for indoor ozone. Shu and Morrison (2012) found that up to 95% of the reactions between DHM and ozone occur on surfaces. This fact has important implications when considering a "personal reactive cloud". DHM might be emitted regularly after application of a body spray, but the majority of reactions between DHM and ozone might not occur until after DHM has sorbed to an indoor surface.

Average DHM concentrations measured in the chamber during trials when the body spray was applied to human subjects varied from 1.1 to 2.3 ppb. These values correspond to the average concentration of DHM in the chamber during the duration of the trial. A maximum, average emission rate, E_{DHM}, can be determined by using the average DHM

concentration and duration of the trial assuming that the deposition of DHM on surfaces is negligible. From the six trials with the body spray applied, the total mass of DHM applied varied from 261 to 559 μg, with an average E_{DHM} equal to 9.9 μg/min. Some of the mass of DHM could have been lost during the subject's transit from the application site to the chamber.

Linalool is a terpenoid alcohol with a floral scent that is found in many of the same products as DHM, including body sprays, shampoos, soaps, and other toiletries (Letizia et al., 2003; Corsi et al., 2007; Chen and Hopke, 2009). Common by-products from ozone/linalool reactions include formaldehyde (Bernard et al., 2012), acetaldehyde, acetone, 4-oxopentanal (Calogirou et al., 1999), and SOA (Chen and Hopke, 2009). In a chamber study testing the kinetics of ozone/linalool reactions, Bernard et al. (2012) found that linalool reacts relatively quickly in the presence of ozone in the gas phase and tends to be consumed near the emission source. Corsi et al. (2007) noted that peak linalool evaporation rates occur 15-75 minutes after application of a model perfume. These two findings imply that in the presence of ozone, a majority of the linalool applied by the body spray will be reacted away after approximately 75 minutes due to gas-phase and surface reactions. Linalool was not detected in the chamber during trials when the body spray was applied to human subjects. This finding suggests that either all of the emitted linalool reacted with ozone or was purged from the chamber due to the high AER.

Ozone Reactivity with Cotton T-Shirts

Two trials occurred during each T-shirt experiment: T-shirts tested without and with the body spray applied. General information for each trial is given in Table 2. Reactions between ozone and compounds present on the T-shirts happened rapidly; minimum ozone concentrations were reached after approximately 30 minutes of exposure.

The T-shirts were left in the chamber for longer than the design time of $3/\lambda$ hours to ascertain if the ozone concentration within the chamber would stabilize or begin to rise if the compounds reacting with ozone on the T-shirts were spent. In some cases, the ozone concentration would rise by only a few ppb after a minimum was reached until establishing a new steady-state ozone concentration. However, in the fourth trial, the ozone reached a minimum and continued to rise until nearly reaching the initial concentration (See Figure 11). For this reason, the value for ΔO_3 in Table 2 was calculated as the initial ozone concentration subtracted by the minimum value recorded during each trial. The variability in ΔO_3 for trials without and with the body spray applied is quite high, but does not appear to be a function of the duration, AER, or the initial ozone concentration. In the trials with the body spray applied, ΔO_3 also does not appear to be a function of the duration, AER, or initial concentration. The mass of body spray applied, however, does seem to increase ΔO_3. The mass of body spray applied in trial 5 was more than double the amount applied in trials 4 and 6, and had the greatest ΔO_3. This finding supports our initial hypothesis that the more body spray applied, the greater the decrease in ozone concentration.

Table 2: Effects of T-shirts in chamber on ozone concentration

Trial	**Body Spray**	**Duration** (min)	**Initial Css** (ppb)	**ΔO_3**[a] (ppb)	**M**[b] (g)	**k_b** (h^{-1})	**k_c** (h^{-1})	**v_p** (m/h)
1	No	78.0	72.4	10.4	-	1.7	0.4	5.9
2	No	63.0	73.5	16.2	-	1.7	1.2	15.8
3	No	69.0	75.6	23.1	-	1.7	0.7	9.5
Average	No	70.0	73.8	16.6	-	1.7	0.8	10.4
4	Yes	69.0	70.2	15.1	2.2	1.7	0.7	9.5
5	Yes	63.0	67.5	17.3	5.6	1.7	1.4	17.8
6	Yes	90.0	71.2	23.0	2.4	1.7	0.8	11.1
Average	Yes	74.0	69.6	18.5	3.4	1.7	1.0	12.8

[a] Difference in initial steady-state ozone concentration and the minimum ozone concentration measured with T-shirts in the chamber
[b] Total mass of body spray applied

An example of the variation in ozone concentration over the duration of one experiment is shown in Figure 7 and is representative of the other two (see Appendix B). Periods when the doors were opened to remove the T-shirts are shown because ozone concentrations decreased slightly from dilution of the chamber air by laboratory air. A similar phenomenon occurred when doors were opened to place T-shirts inside the chamber, but the decrease in ozone concentration from dilution is negligible compared to the contribution from reactions with the T-shirts, and the door was only opened for a few seconds. Additionally, any decrease in ozone concentration by dilution would be negligible after running the experiment for at least $3/\lambda$ hours.

Reactions between ozone and compounds present on the T-shirts happened rapidly; minimum ozone concentrations were reached after approximately 30 minutes of exposure. In some cases, the ozone concentration would rise by a few ppb after a minimum was reached until establishing a new steady-state ozone concentration. However in the fourth trial, the ozone reached a minimum and continued to rise until nearly reaching the initial concentration. For this reason, ΔO_3 was calculated as the initial ozone concentration subtracted by the minimum value recorded during each trial. The variability in ΔO_3 for trials without and with the body spray applied is quite high, but does not appear to be a function of the duration, AER, or the initial ozone concentration. In the trials with the body spray applied, ΔO_3 also does not appear to be a function of the duration, AER, or initial concentration. The mass of body spray applied, however, does seem to increase ΔO_3.

The average decay rates to the T-shirts, κ_c, without and with the body spray applied were 0.8 h^{-1} and 1.0 h^{-1}, respectively. While these values indicate that the T-shirts applied with the body spray are more reactive, the difference is not significant. This small difference could be attributed to a number of confounding variables other than differences in the mass application of the body spray, such as the accuracy of the ozone analyzers, variations in the amount of ozone generated within the supply duct, or fluctuations in the ozone concentration within the lab space. The ozone analyzers have an accuracy of ±1.0% over the range of 0 - 200 ppb. Barring measurement errors, the ozone supplied into the chamber might have fluctuated over the course of the experiment due to variations in either the ozone generated or concentration in the supply air. Any fluctuation in the ozone concentration in the air supplied to the duct from the laboratory would cause an increase in the ozone concentration entering the chamber because the ozone generator would further increase the concentration by a constant value. For the first three experiments, an additional ozone monitor (2B Technologies, Model 202 Ozone Monitor) was set up to measure the

ozone concentration in the laboratory. Over the course of one experiment, the ozone concentration in the lab space varied from 1.0 to 20.4 ppb. However, background (laboratory) ozone concentrations typically varied by no more than 1 to 5 ppb during experiments.

By estimating the surface area of a medium-sized T-shirt, the deposition velocities to a single T-shirt were calculated according to Eq. 5. Average deposition velocities were 10.4 m/h and 12.8 m/h without and with the body spray applied, respectively. Studies have shown that ozone readily reacts with cotton materials (Grøntoft and Raychaudhuri, 2004; Coleman et al., 2008a; Rai et al., 2014). An early study found an average ozone deposition velocity to cotton muslin of 3.9 m/h (Sabersky et al., 1973). Since then more sophisticated studies have been performed in controlled settings. In a series of two chamber experiments, Coleman et al. (2008a) tested ozone deposition to laundered cotton clothing fabric while considering aging and reported an average deposition velocity of 10.8 m/h. In an experiment similar to the first trial performed in this study, Rai et al. (2014) measured the ozone uptake to laundered and soiled T-shirts and found a deposition velocity of 4.7 m/h to the laundered T-shirt. Di et al. (2017b) measured an average ozone deposition velocity to a laundered cotton vest of 18.4 m/h using a laboratory emission cell. The variability in ozone deposition velocity might be due to the mixing conditions within the indoor environment. A high AER means the space will have greater turbulent kinetic energy, causing an increase in the uptake of ozone due to increased transport-limited deposition velocity (See Eq. 6). The difference in deposition velocity between this study and that performed by Rai et al. (2014) can be explained by the value for AER. T-shirt experiments in this study were conducted at an AER of 6 h^{-1} while Rai et al. (2014) used a far smaller value of 0.5 h^{-1}. Their experiments may have had a greater transport resistance to ozone removal i.e. greater $1/v_t$ in Eq. 6.

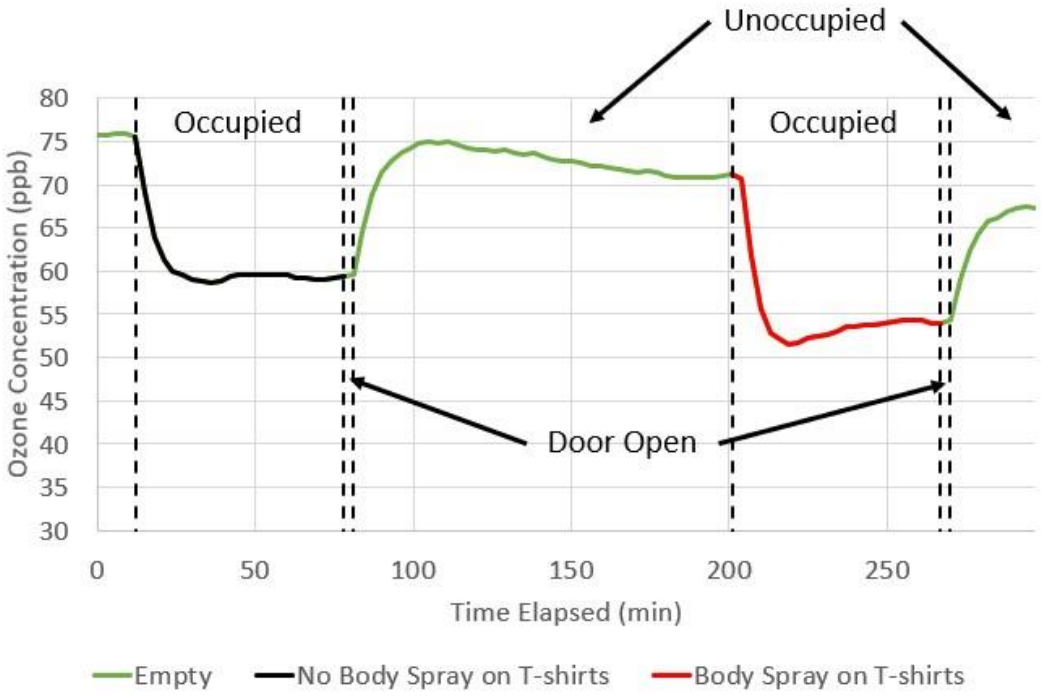


Figure 7: Example ozone concentration profile during T-Shirt experiment

Ozone Reactivity with Humans

The results from the chamber experiments with Subjects 1 and 2 are shown in Tables 3 and 4, respectively. In contrast to the results of the T-shirt experiments, the initial and final steady-state ozone concentrations are given because ΔO_3 was calculated by the difference in these two concentrations rather than by identifying the minimum concentration during the trial periods. Experiments were conducted at an AER of 4 h^{-1} unless otherwise noted.

Table 3: Ozone concentrations, decay rates, and deposition velocities to Subject 1

Trial	**Body Spray**	**Duration** (min)	**Initial Css** (ppb)	**Final Css** (ppb)	**M** (g)	k_b (h^{-1})	k_p (h^{-1})	v_p (m/h)
1[c]	No	33	61.8	45.6	-	1.7	2.8	14.7
2	No	48	67.3	40.1	-	3.5	2.8	14.9
3	No	39	64.9	38.7	-	2.2	4.1	21.5
Average	-	40	64.7	41.5	-	2.5	3.2	17.0
4[c]	Yes	30	58.0	45.5	1.1	1.7	2.2	11.4
5	Yes	36	64.1	40.7	1.3	3.9	1.8	9.6
6	Yes	42	60.3	35.4	1.3	2.4	4.1	21.6
Average	-	36	60.8	40.5	1.2	2.6	2.7	14.2

[c] Experiments were conducted at an AER of 6 h^{-1}

Table 4: Ozone concentrations, decay rates, and deposition velocities to Subject 2

Trial	**Body Spray**	**Duration** (min)	**Initial Css** (ppb)	**Final Css** (ppb)	**M** (g)	k_b (h^{-1})	k_p (h^{-1})	v_p (m/h)
1	No	54	49.0	30.1	-	2.5	3.5	17.0
2	No	33	52.4	38.0	-	2.5	2.0	9.6
3	No	42	60.0	34.4	-	2.7	4.0	19.4
Average	-	43	53.8	34.2	-	2.6	3.2	15.3
4	Yes	45	46.4	31.2	0.8	2.5	2.7	12.8
5	Yes	36	60.8	38.7	1.2	2.5	3.2	15.3
6	Yes	39	58.9	35.2	1.2	2.7	3.6	17.4
Average	-	40	55.4	35.0	1.1	2.6	3.2	15.2

The ozone concentration profile from one experiment for Subject 1 is shown in Figure 8. The results from the other five experiments are provided in Appendix B. Times when the door was open to allow the occupant to exit are shown. Trial durations for the human subject experiments are, on average, shorter than those for T-shirts because experiments were stopped when the 3-minute averaged ozone concentrations differed by less than 2 ppb.

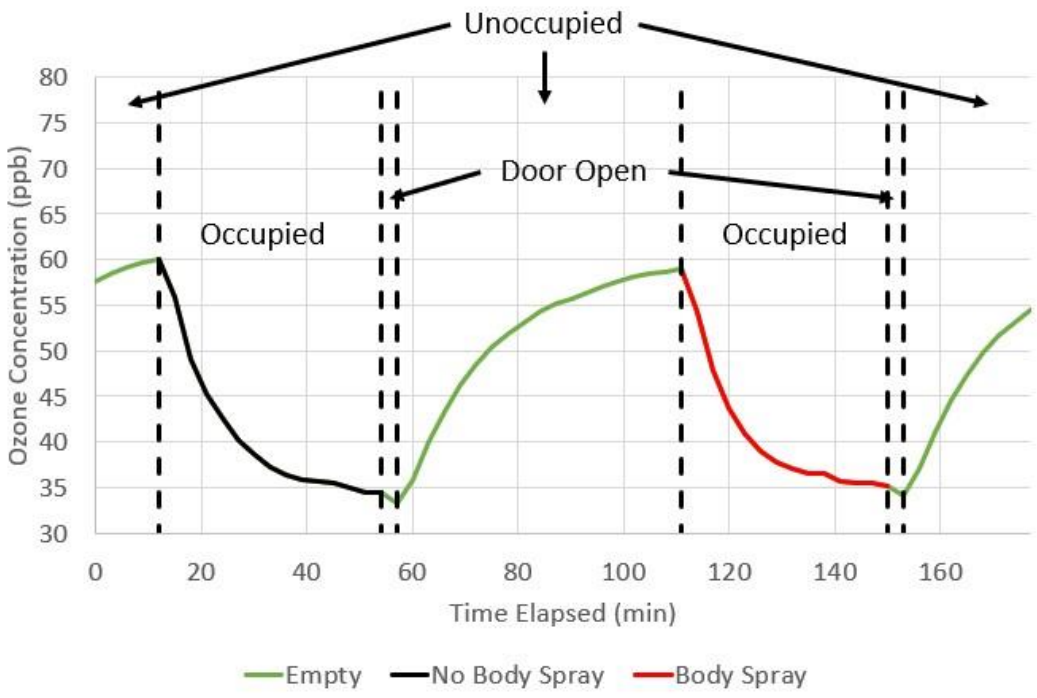


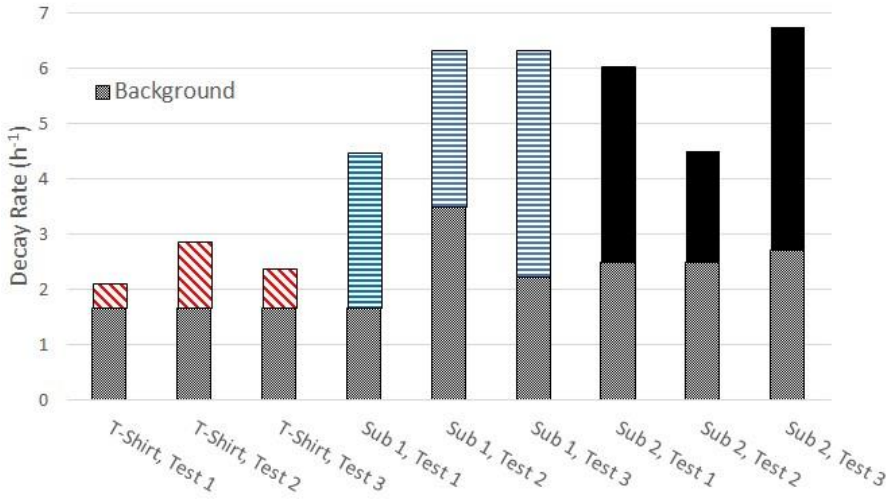
Figure 8: Example ozone concentration profile during occupant experiment

During the first two unoccupied times, κ_b was calculated and subtracted from κ obtained during occupied times to get κ_p. Results from these calculations are shown in Figure 9 and are compared between both subjects and κ_c from the T-shirt experiments. Every calculated value of κ_c was less than the minimum κ_p from either subject. confirming previous literature that shows humans can be large sinks for ozone. Wisthaler and Weschler (2010) estimated that humans can represent anywhere from 10% to 25% of the total ozone uptake in buildings. Figure 9 indicates that total ozone removal might be higher. Without the body spray applied, ozone removal by reactions with subjects accounted for between 44% and 65% of the total removal.

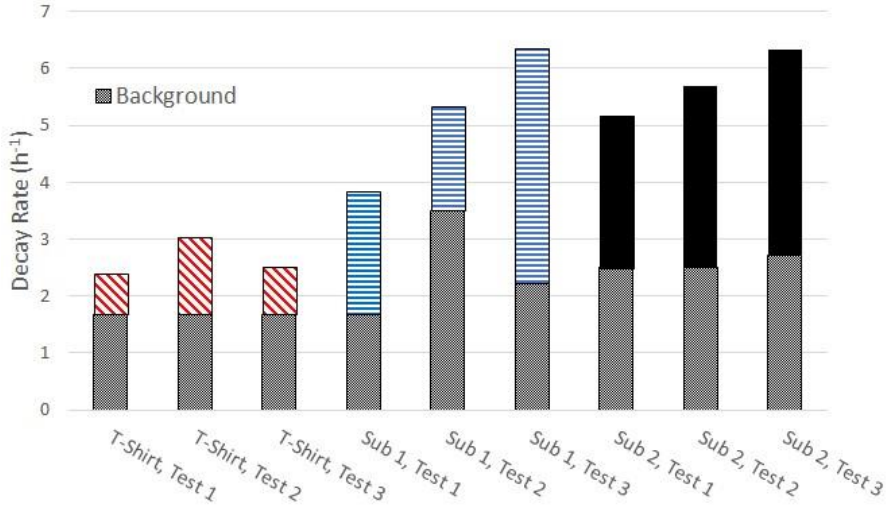
Both subjects had an average κ_p of 3.2 h^{-1} without the body spray applied. In a similar study to the trials performed without the body spray applied, Wisthaler and Weschler (2010) reported κ_p values for two adult men in an office-sized chamber of 1.7 h^{-1}

and 2.0 h^{-1} in two separate scenarios ventilated at an AER of 1 h^{-1}. Rim et al. (2009) determined similar values for κ_p between 1.35 to 1.62 h^{-1} when simulating a human body and heat output in a computational fluid dynamics (CFD) model using AERs between 0.71 and 0.86 h^{-1}. Results from this study show that humans are potentially more reactive than the previously mentioned literature sources, even without application of a body spray. The increased reactivity is again influenced by the greater AER of 4 h^{-1} used in this study.

Average κ_p were very consistent for each subject without and with the body spray applied. When the body spray was applied, the average κ_p values were 2.7 h^{-1} and 3.2 h^{-1} for Subject 1 and Subject 2, respectively.



(a) No body spray applied



(b) Body spray applied

Figure 9: Comparison of ozone decay rates without and with the body spray applied. The height of each bar represents the total ozone decay rate, κ; the bottom portion represents decay just to background surfaces, κ_b; and the remainder is the decay rate to a single occupant or T-shirt.

Using the height and weight of the two subjects, their body surface area (BSA) was estimated by the Du Bois formula given in Eq. 7, where W is the subject's mass (kg) and

H their height (cm). Subject 1 weighed 86 kg and was 182 cm tall while Subject 2 weighed 99 kg and measured 188 cm tall.

$$BSA = 0.0007185W^{0.425}H^{0.725} \quad (7)$$

Deposition velocities were calculated using the BSA for each subject according to Eq. 5 and are summarized in Tables 3 and 4. Comparisons between the average deposition velocities calculated for each subject and the T-shirt experiments without and with the body spray applied are shown in Figure 10. Several researchers have found ozone deposition velocities attributed to humans in the range of 5.4 m/h to 22.3 m/h using a variety of experimental procedures (Fadeyi, 2015 and references therein). Many of these studies used controlled environmental chambers. Wisthaler and Weschler (2010) measured ozone deposition velocities of 14.4 to 18.0 m/h in a simulated office environment ventilated at 1 h^{-1}. Similarly, Fadeyi et al. (2013) modeled their chamber to represent a typical office space and found that at a ventilation rate of 1 h^{-1}, the ozone deposition velocity to humans ranged between 14.4 to 22.3 m/h. Yang et al. (2016) extracted skin oil from worn clothing and exposed it to ozone in a chamber ventilated with an AER of 1 h^{-1} and calculated a value of 5.4 m/h for ozone deposition to human skin oil. Few studies have also used field experiments to determine the ozone deposition velocity to human skin. Fischer et al. (2013) found an average ozone deposition velocity to students in a naturally ventilated classroom of 16.2 m/h. In an effort to validate these results, researchers have also developed models using CFD software. Rim et al. (2018) tested multiple scenarios varying the ventilation type/rate, the reaction probability, and the ozone concentration and found deposition velocities to a simulated human ranging from 2.4 m/h to 11 m/h. Results from this study

are consistent with those in the literature, even when considering the trials performed with the body spray applied.

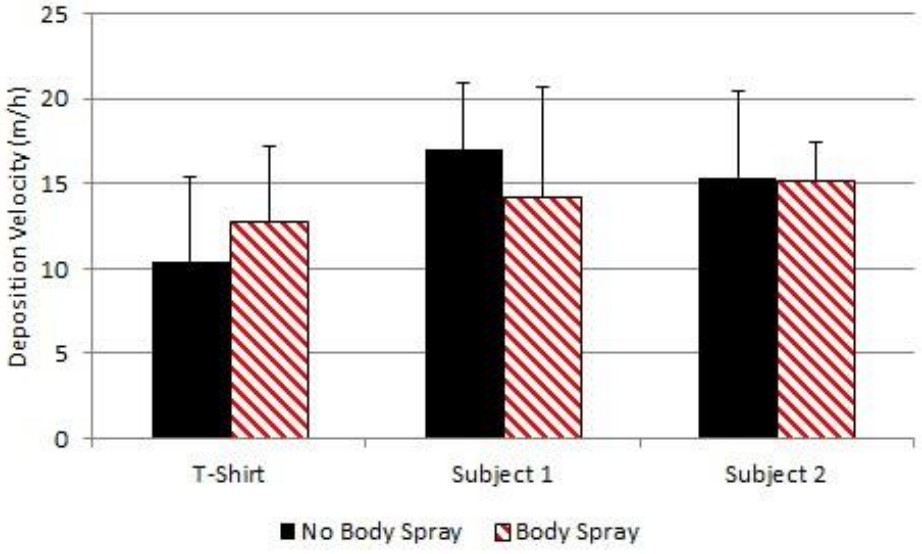


Figure 10: Average deposition velocities without and with the body spray applied from the T-shirt experiments and those with Subject 1 and Subject 2. Information on the surface areas of the T-shirts and subjects can be found in the supplemental information.

Based on the concentration profile in Figure 8 and the deposition velocities without and with the body spray applied, application of the body spray does not seem to alter the reactivity of the occupant to a significant level. Figure 10 shows that on average, the subjects actually tended to be less reactive when the body spray was applied. Decreased reactivity could be due to competing reactions between ozone and molecules from the body spray and between ozone and human skin lipids, or because the concentration of terpenes is too low to significantly alter the ozone concentration. Corsi et al. (2007) found that linalool concentrations at its odor threshold, approximately 1000 ppb, reduced the ozone concentration by only 1%. Based on the amount of body spray applied and the percent by

mass of linalool, the maximum linalool concentration in the chamber would have been approximately 1100 ppb. Assuming this concentration remained constant throughout the experiment, gas-phase reactions between ozone and linalool would only account for 1% of the decrease in ozone concentration. However, surface reactions between ozone and sorbed terpenes typically account for a larger proportion of the ozone uptake. Shu and Morrison (2012) found that 95% of the reactions between ozone and DHM occur on surfaces, and Springs et al. (2011) found that surface-specific reaction probabilities for d-limonene are 10 to 100 times greater than those in the gas-phase. Even though compounds are continuously emitted after applying a body spray, reactions in the gas phase might not effectively alter ozone concentrations near building occupants. According to Weschler (2000), the half-life for d-limonene, one of the more reactive terpenes, in the presence of 30 ppb of ozone is about 0.75 hours. At an AER of 4 h^{-1}, the air will be recycled every 0.25 hours and reactions between compounds like d-limonene and ozone will not have a large effect on the bulk ozone concentration.

The lack of gas-phase chemistry means surface reactions between reactive molecules on human/clothing surfaces and ozone represent the largest potential sink for indoor ozone. Applying a body spray adds to the number of reactive compounds present on human surfaces. The potential for ozone uptake is larger because of this fact, but because human skin is so reactive with ozone, ozone removal to human surfaces tends to be transport-limited (Rim et al., 2018). Additionally, ozone uptake might be slowed due to steric hindrance of the body spray's primary constituent: DHM. Research has shown that DHM molecules might fold over when sorbed to surfaces, effectively covering the carbon-carbon double bond that ozone reacts with so favorably (Forester et al., 2006; Ham and Wells, 2009). Therefore, ozone is primarily reacting with skin lipids rather than the compounds from the body spray sorbed to the subject's skin and clothing. This means that

surface reactions on human skin are not going to be significantly higher with the body spray applied versus without.

CONCLUSION

In this study, the effects of body sprays on the ozone deposition velocity to human subjects were tested in a controlled, environmental chamber. Subjects without and with the body spray entered into the chamber when the ozone concentration was around 60 ppb. Decreases in ozone concentration were measured during these periods in order to calculate ozone decay rates and deposition velocities. Similar experiments were also done with once-washed T-shirts. Results from the two human subjects are summarized in Table 3 and 4 while results from the T-shirt experiments are given in Table 2. The results from this study indicate that body sprays do not appreciably alter the ozone reactivity near or on clothing/human surfaces. Measurements of the VOCs during the trials when a body spray was applied indicate that ozone chemistry is occurring, but the concentrations of reactive species like linalool are too low to affect a measurable change in the bulk ozone concentration. However, near-head chemistry is still a topic of concern since ozone/terpene reactions can produce sensory irritants and more harmful compounds like formaldehyde. Additional P_eCPs such as deodorants or colognes/perfumes with different chemical compositions should be tested to ascertain how these products differ from the one tested in this study and to see if these other products are capable of reducing indoor ozone concentrations. Future studies should consider the effects of AER on ozone uptake to humans without and with these different P_eCPs and how air flow around a human subject might alter the types and concentrations of by-products generated from reactions between ozone and terpenes found in scented P_eCPs.

Appendix B: Supplementary Information

Body Spray Compositions

Composition analyses of five body sprays marketed to males were conducted as an initial screening to determine which would be the most reactive. Terpenes and terpene alcohols react at rates comparable to the air exchange rate in a home (Weschler, 2000). Therefore, the body spray that contained the highest percent by mass of reactive terpene and terpene alcohol species was the body spray used in the experimental phase of this study. Tables 5 through 9 highlight various components of the five different body sprays, including terpenes and terpene alcohols. Only compounds that could be identified with a quality of 80% or higher by GC/MS are shown. Boldfaced compounds in Tables 5 through 9 are terpenes or terpene alcohols.

Table 5: Percent by mass of compounds identified by GC-MS for Body Spray 1

Compound	**Percent by Mass**	**CAS Number** [1]
2-Methylhexane	1.08	000591-76-4
3-Methylhexane	1.40	000589-34-4
Heptane	1.69	000142-82-5
Toluene	0.24	000108-88-3
hexamethylcyclotrisiloxane	0.18	000541-05-9
p-Xylene	0.42	000106-42-3
***α*-Pinene**	0.11	007785-70-8
m-Bromofluorobenzene	2.36	001073-06-9
m-Ethylmethylbenzene	0.16	000620-14-4
Decane	0.49	000124-18-5
as-Trimethylbenzene	0.43	000095-63-6
d-Limonene	0.07	005989-27-5
Isooctanol	0.44	026952-21-6
Undecane	0.38	001120-21-4
Dipropylene glycol	1.91	000110-98-5
Dihydromyrcenol	7.15	018479-58-8
Linalool	1.06	000078-70-6
Dodecane	0.08	000112-40-3
Anthranilic acid	1.98	007149-26-0
***α*-Terpinyl Acetate**	0.24	000080-26-2
Geranyl Acetate	0.25	000105-87-3
Damascenone A	0.18	023696-85-7
α-Damascone	0.10	031089-90-4
Allyl cyclohexanepropionate	0.77	002705-87-5
***α*-Cedrene**	0.40	000469-61-4
Butylated Hydroxytoluene	2.88	000128-37-0
α Isomethyl Ionone	3.95	000127-51-5
β-Irone	0.18	000079-70-9
Coumarin	1.57	000091-64-5
Lilial	4.93	000080-54-6

[1] Unique chemical identifying number assigned to every compound by the Chemical Abstracts Service (CAS)

Table 6: Percent by mass of compounds identified by GC-MS for Body Spray 2

Compound	**Percent by Mass**	**CAS Number**
Toluene	0.24	000108-88-3
hexamethylcyclotrisiloxane	0.29	000541-05-9
***α*-Pinene**	0.15	002437-95-8
m-Bromofluorobenzene	1.94	001073-06-9
Decane	1.10	000124-18-5
Benzaldehyde	0.17	000100-52-7
***β*-Ocimene**	0.26	013877-91-3
Isooctanol	0.53	026952-21-6
Dihydromyrcenol	20.1	018479-58-8
Linalool	5.90	000078-70-6
Acetic Acid	0.85	067634-00-8
Anthranilic acid	8.34	007149-26-0
Citral	0.09	000106-26-3
2,6-Dimethyl 2,6-octadiene	0.61	002792-39-4
Neryl acetate	0.14	000141-12-8
α-Terpinyl Acetate	0.23	000080-26-2
Geranyl Acetate	0.23	000105-87-3
trans-*α*-Damascone	0.18	024720-09-0
Caryophyllene	0.34	000087-44-5
β-Cymene	0.27	000535-77-3
Coumarin	0.61	000091-64-5
Cashmeran	0.52	033704-61-9
Helional	0.21	001205-17-0
cis-3-Hexenyl Salicylate	0.44	065405-77-8
13-Methyloxacyclotetradecane-2,11-dione	1.00	074685-36-2

Table 7: Percent by mass of compounds identified by GC-MS for Body Spray 3

Compound	**Percent by Mass**	**CAS Number**
Toluene	0.20	000108-88-3
α-Methylcyclopentanone	0.20	001120-72-5
m-Bromofluorobenzene	1.68	001073-06-9
d-Limonene	0.41	000138-86-3
Dihydromyrcenol	22.0	018479-58-8
Linalool	4.58	000078-70-6
β-Thujone	0.17	000471-15-8
(-)-Alcanfor	0.07	000464-48-2
α-Methylbenzyl acetate	0.56	000093-92-5
Decanal	0.44	000112-31-2
Acetic Acid	0.45	067634-00-8
3,7-dimethyloct-2-en-1-ol	1.26	040607-48-5
D-Carvone	0.13	002244-16-8
cis-4-tert-butylcyclohexyl acetate	0.82	010411-92-4
4-tert-Butylhexahydrophenyl acetate	1.74	032210-23-4
***β*-Patchoulene**	0.07	000514-51-2
Dodecanal	0.39	000112-54-9
trans-*α*-Damascone	0.16	024720-09-0
***α*-Guaiene**	1.31	003691-12-1
Thujopsene	0.69	000470-40-6
Napthalene	0.12	000473-13-2
α-Bulnesene	0.66	003691-11-0
α Isomethyl Ionone	0.34	000127-51-5
β-Ionone	1.61	014901-07-6
Cuparene	0.07	016982-00-6
Lilial	5.53	000080-54-6
Cyclopentaneacetic Acid	0.90	024851-98-7
Patchouli Alcohol	0.27	005986-55-0

Table 8: Percent by mass of compounds identified by GC-MS for Body Spray 4

Compound	**Percent by Mass**	**CAS Number**
Toluene	0.33	000108-88-3
hexamethylcyclotrisiloxane	0.24	000541-05-9
α-Pinene	0.14	007785-70-8
Cyclohexanone	0.18	000108-94-1
m-Bromofluorobenzene	3.03	001073-06-9
d-Limonene	0.11	005989-27-5
Dihydromyrcenol	23.5	018479-58-8
Linalool	4.88	000078-70-6
Decanal	0.38	000112-31-2
Citronellol	1.94	001117-61-9
3,7-Dimethyl-2,6-octadien-1-ol	0.57	000624-15-7
Damascenone A	0.28	023696-85-7
α-Cedrene	0.18	000469-61-4
Isocaryophyllene	0.37	1000140-07-2
Coumarin	0.68	000091-64-5
Cashmeran	1.40	033704-61-9
Cyclopentaneacetic Acid	2.81	024851-98-7
Octanal	0.46	000101-86-0
Decylenic alcohol	0.54	013019-22-2

Table 9: Percent by mass of compounds identified by GC-MS for Body Spray 5

Compound	**Percent by Mass**	**CAS Number**
Toluene	0.47	000108-88-3
hexamethylcyclotrisiloxane	0.35	000541-05-9
α-Pinene	0.22	007785-70-8
Cyclopentanone	0.32	001120-72-5
m-Bromofluorobenzene	3.31	001073-06-9
Ethanol	1.58	000111-90-0
Dihydromyrcenol	7.40	018479-58-8
Linalool	3.49	000078-70-6
Citronellol	1.77	001117-61-9
Anthranilic acid	5.25	007149-26-0
Citral	0.21	000141-27-5
Tetradecane	0.33	000629-59-4
Geranyl Acetate	0.27	000105-87-3
β-Patchoulene	0.18	000514-51-2
α-Guaiene	1.10	003691-12-1
Caryophyllene	0.29	000087-44-5
Seychellene	0.54	020085-93-2
α-Bulnesene	1.44	003691-11-0
Cashmeran	1.68	033704-61-9
Patchouli Alcohol	0.90	005986-55-0

OZONE CONCENTRATION PROFILES FROM T-SHIRT EXPERIMENTS

Figures 11 through 13 show the variation in ozone concentration during trials without and with the body spray applied to three T-shirts. Regions following the occupied periods correspond to when the chamber door was opened to remove the T-shirts. For T-shirt experiments, the ozone decay rate was determined by comparing the ozone concentration at the start of "T-shirt in" periods to the minimum concentration measured during these periods.

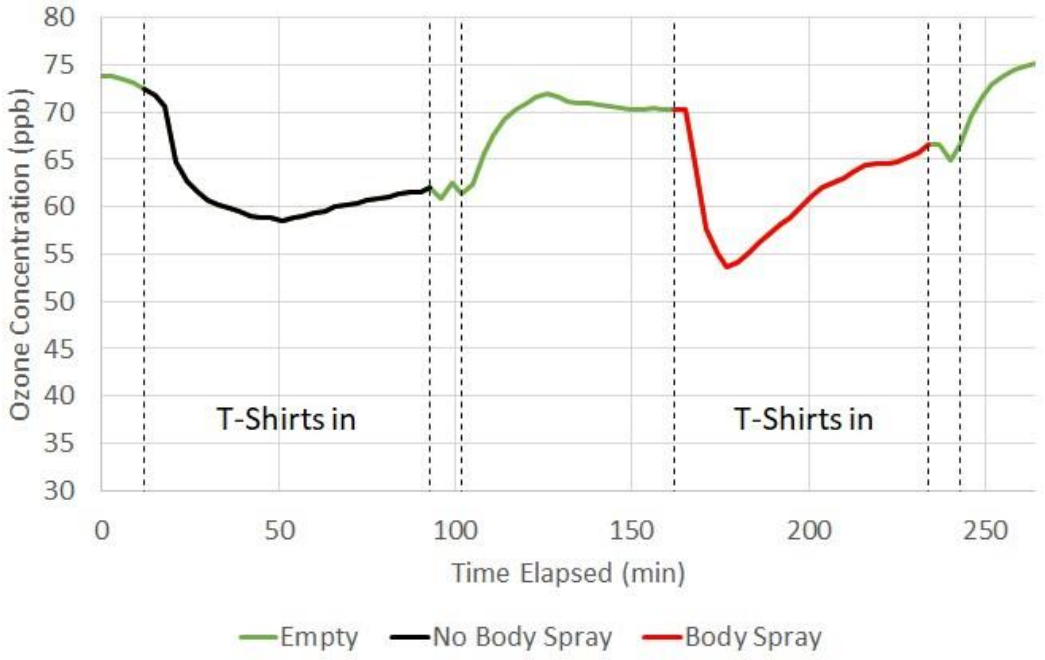


Figure 11: Ozone concentration profile during the first T-shirt experiment

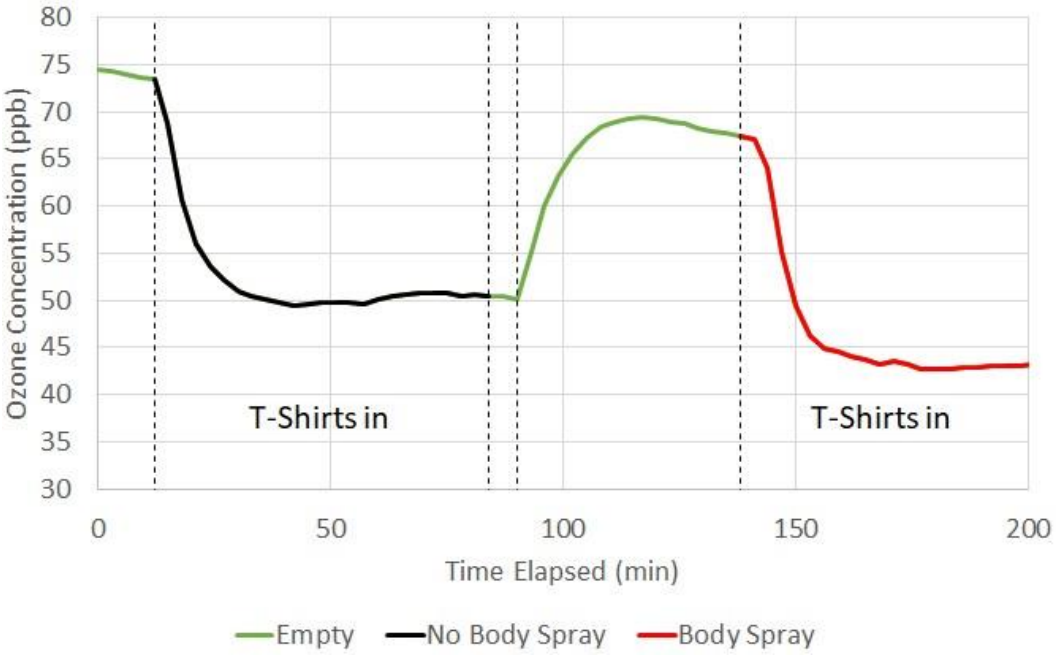


Figure 12: Ozone concentration profile during the second T-shirt experiment

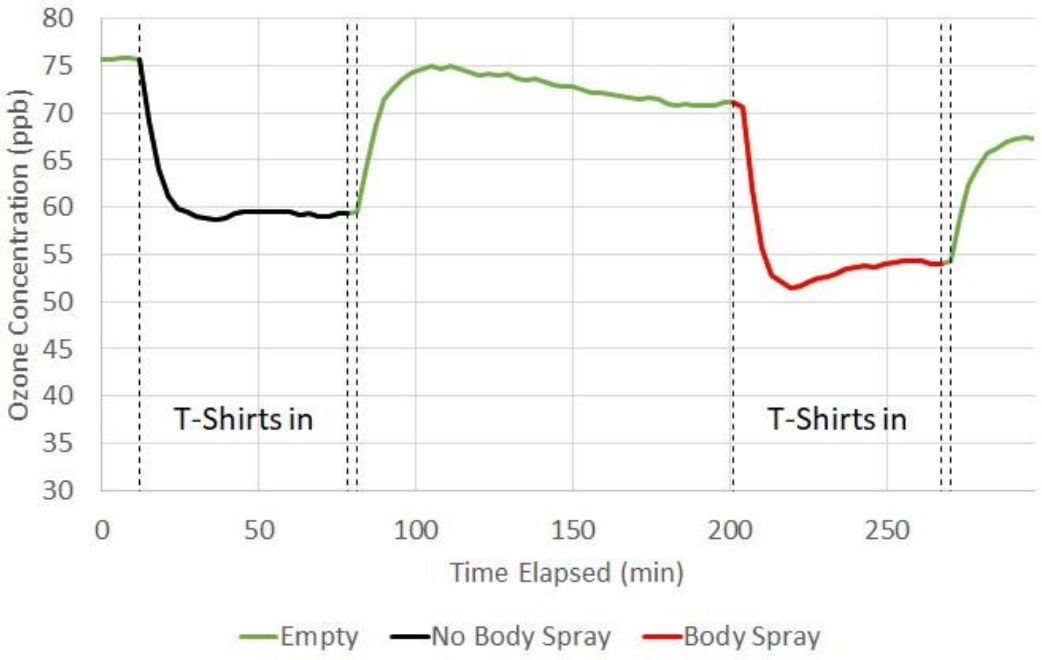


Figure 13: Ozone concentration profile during the third T-shirt experiment

OZONE CONCENTRATION PROFILES FROM EXPERIMENTS WITH HUMAN SUBJECTS

Figures 14 through 19 illustrate the ozone concentration profile during experiments with human subjects. Regions marked off by dashed lines that occur after occupied periods are times when the door remained open. In some cases, the door remained open for extended periods of time after testing was over because the subject remained inside. This allowed the laboratory air to dilute the ozone concentration in the chamber quite significantly (see Figures 14, 15, and 16).

Moments during occupied and unoccupied periods when the ozone concentration increased slightly (see Figures 16 and 17) are due to differences in the laboratory ozone concentration. Laboratory ozone concentrations generally varied by no more than 5 ppb, but during some experiments varied up to almost 20 ppb. No control was implemented at the inlet to the chamber to ensure a constant ozone concentration was supplied the space.

While the ozone generator provided a constant source of ozone, variability in the laboratory ozone concentration altered the ozone concentration measured at the inlet and in middle of the chamber.

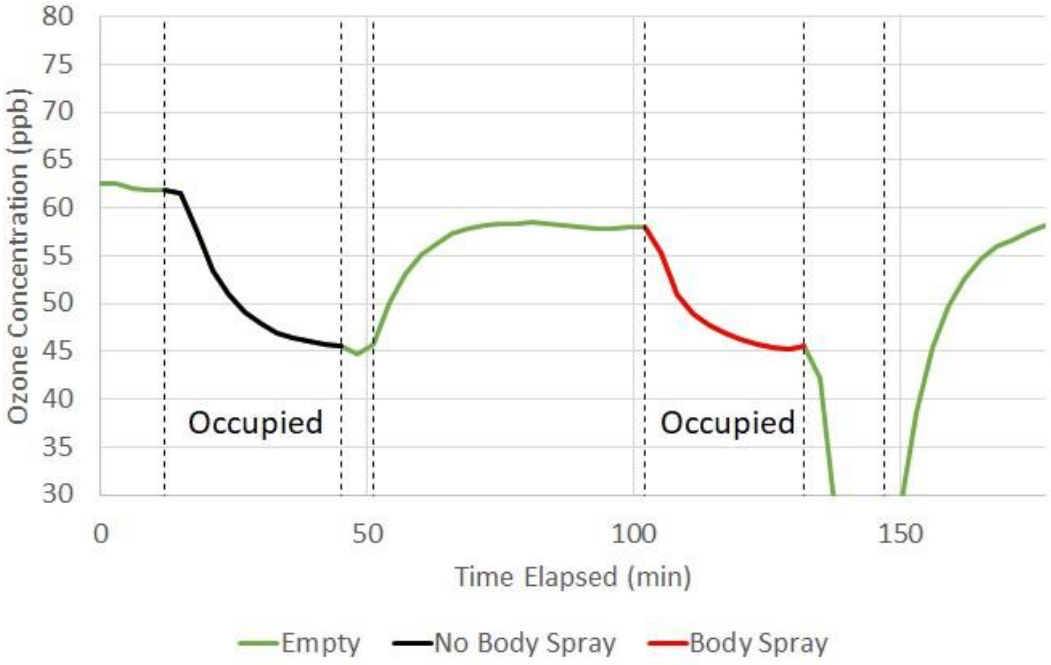


Figure 14: Ozone concentration profile during the first experiment with Subject 1

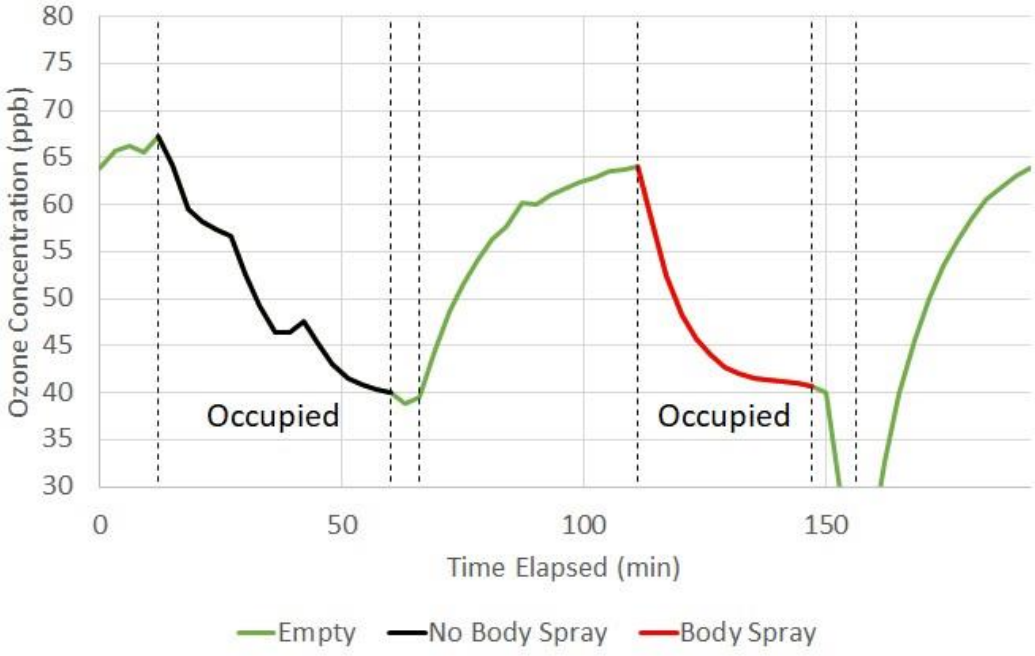


Figure 15: Ozone concentration profile during the second experiment with Subject 1

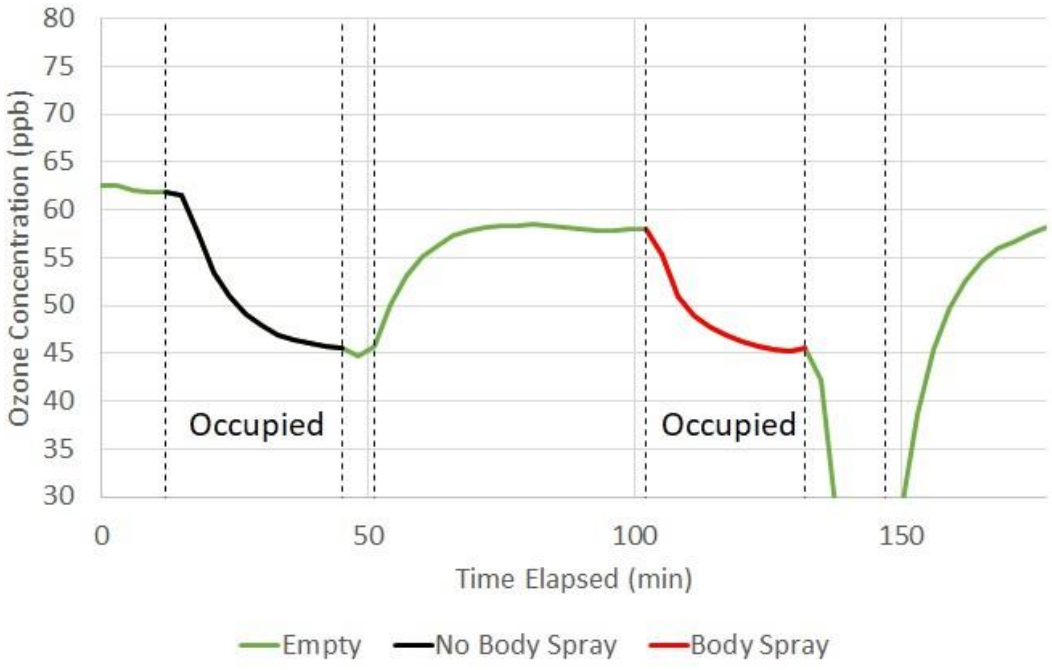


Figure 16: Ozone concentration profile during the third experiment with Subject 1

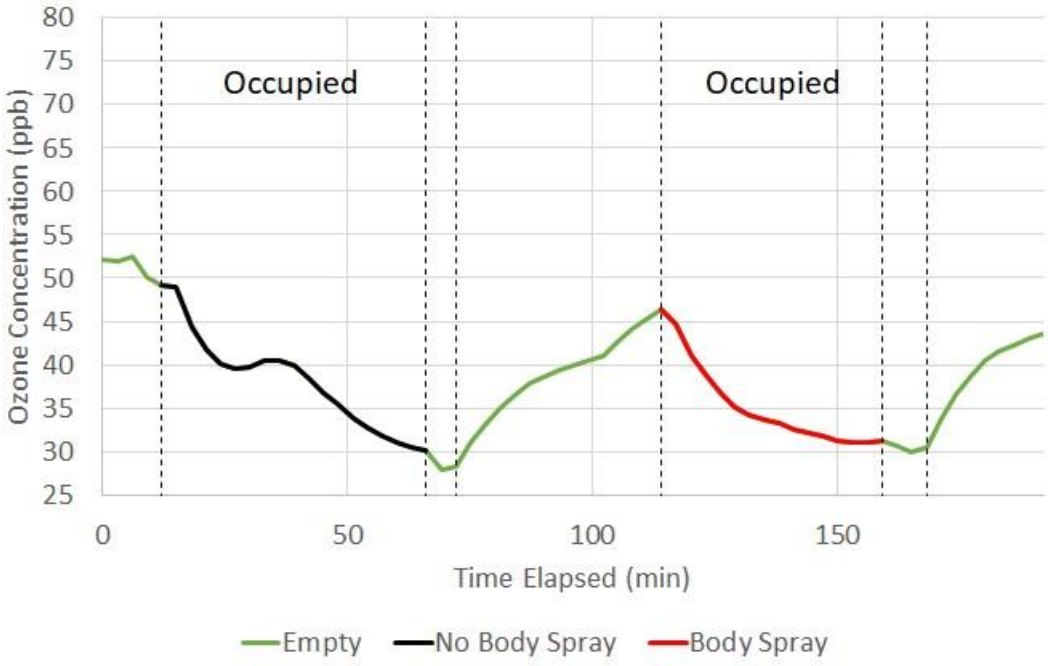


Figure 17: Ozone concentration profile during the first experiment with Subject 2

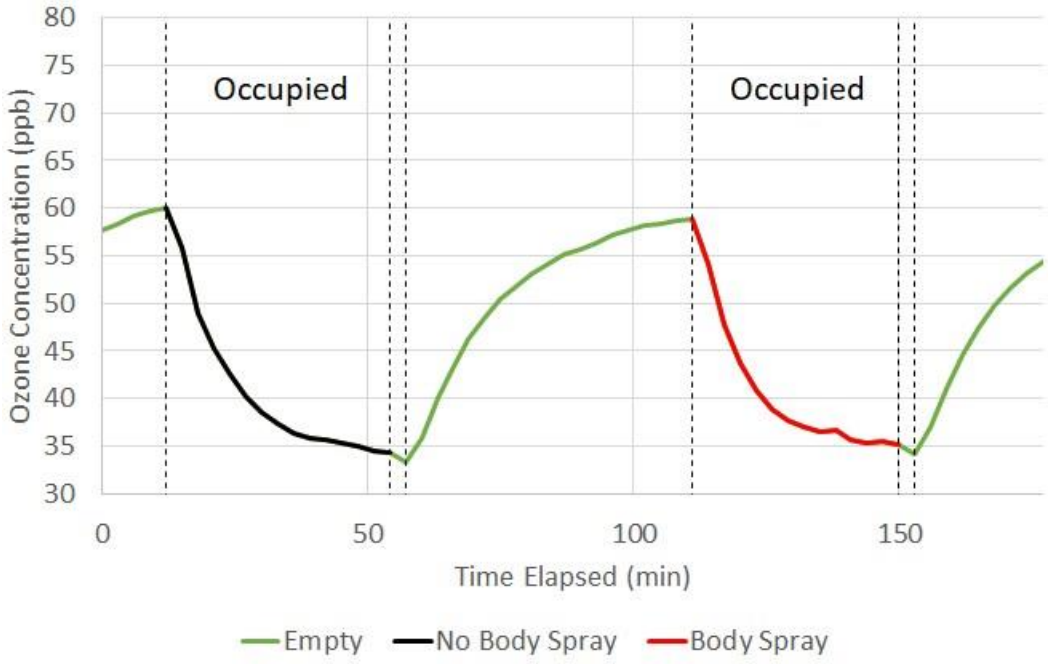


Figure 18: Ozone concentration profile during the second experiment with Subject 2

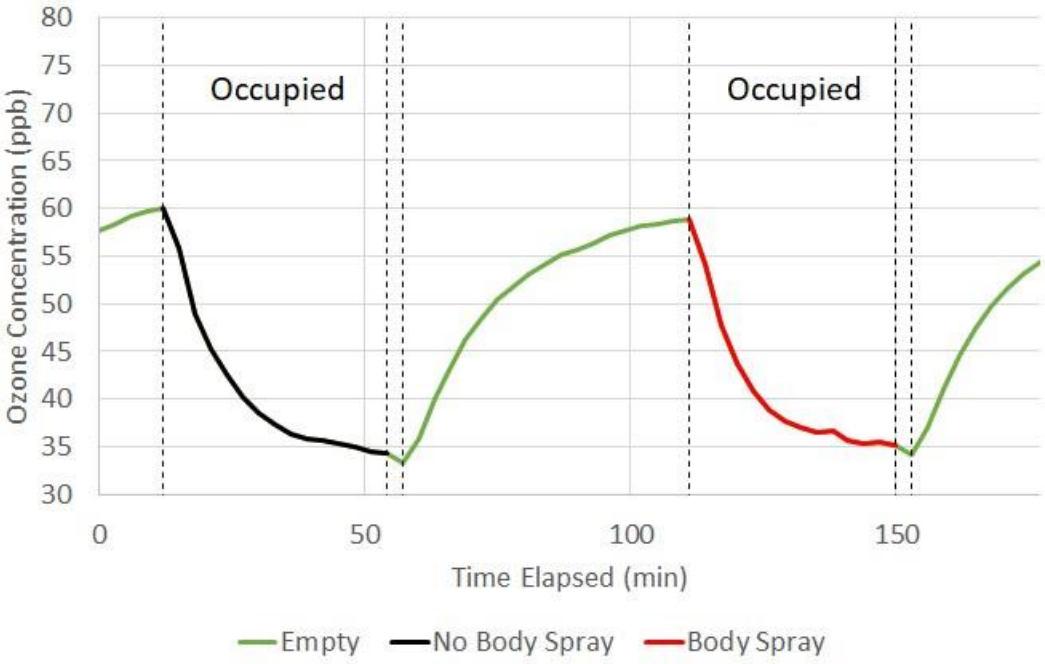


Figure 19: Ozone concentration profile during the third experiment with Subject 2

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